



# CHEMICAL ABSTRACTS

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## 1—APPARATUS

C. G. DERICK

Applications of vapor pressure measurements. H. S. AND MARY D. DAVIS. *Ind. Eng. Chem.* 15, 1075-7 (1923); cf. C. A. 12, 1818, 2076. A description of improvements tending to lessen breakage and make more flexible an app. previously patented and described by the authors. This app. is used for measuring vapor pressures and may be used for checking the work of an absorption plant. P. D. V. MANNING

An improved method for the separation of gas mixtures. MARTIN SHEPHERD AND FRANK PORTER. *Ind. Eng. Chem.* 15, 1143-6 (1923).—By using a well designed all-glass app. with no rubber connections, and with accurately ground and suitably lubricated stopcocks, and eliminating capillary dead spaces by Hg displacement, etc., it was possible to sep. a Petrolia natural gas into (CH<sub>4</sub>, N<sub>2</sub>, He), C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub> and higher hydrocarbon fractions, quickly and accurately. Liquid air was the refrigerant used, and successive fractions were obtained at -183, -145 to -150, and -120°. With not more than 3 distns. for each component the errors are of the approx. magnitude 0.1%, or about the same as the error involved in estg. vols. with the app. used. Analytical values obtained by combustion with a Pt helix deviate about 5% from the true values detd. as above, owing to the incomplete combustion of C compds. in a wet natural gas, and to errors introduced by the presence of higher hydrocarbons in the gas being burned. The same app. serves to prep. gases in the highest state of purity, as indicated by vapor pressure tests made upon them. W. C. BHAUGH

Cellulose acetate as material for preparation of ultrafilters. R. FRICKE AND P. KLEMP. *Kolloid Z.* 33, 161-8 (1923).—Besides the methods of prep. and properties of the filters, the chem. and phys. properties of commercial cellulose acetate were investigated insofar as these affected the prep. of filters. Ultrafilters were prep. by dissolving 3-10 g. commercial cellulose acetate, found by analysis to be somewhat less than triacetyl, in 100 cc. of solvent (1 vol. of 96% alc. + 9 vol. of CHCl<sub>3</sub>). Five cc. of this soln. was poured on a glass plate 8 cm. in diam. and uniformly distributed by tilting the plate to and fro in an atm. of CHCl<sub>3</sub>. After being dried in the air (8-35 min.) to the desired thickness, the plate was immersed in 96% alc. for about 1 min. before the membrane was removed and washed with water. The filter was a transparent or slightly white membrane. It was not so easily torn or broken as the collodion or De Haen filter. No fungus growth was observed. The thickness of the filter depended on the concn. of the cellulose acetate and the time of drying. The velocity of filtration was greatly increased by laying the membrane on an ordinary filter paper in the ultrafiltration app. The size of the pores can be varied by varying the method of prep. and the filters can be used to filter colloidal solns. contg. different sized particles. When heated dil. acids slowly and dil. alkalis rapidly split off HOAc. In the cold after several days in 0.1 N KOH, a considerable quantity of the acetyl groups had split off but in 0.1 N HCl only an insignificant amt. of HOAc was found. When the cellulose acetate was boiled with H<sub>2</sub>O under a reflux condenser and the very weak acid soln. pressed out, further effect of either H<sub>2</sub>O or dil. acid on the concn. was decreased. H. M. McLAUGHLIN

Fuel oil viscometers. W. H. HERSCHEL. *Chem. Met. Eng.* 26, 1175 (1922).—After making the Couette correction ( $0.311 \times \text{diam.}$ ) and the kinetic energy correction coeff. (1.128) the equation for the normal Saybolt furol viscometer is *kinematic viscosity* =  $0.0220t - (2.03/t)$ . The corresponding equation for the Redwood-Admiralty viscometer is *kinematic viscosity* =  $0.0239t - (0.403/t)$ . By using the equation for the Saybolt Universal viscometer, *kinematic viscosity* =  $0.00229t - (1.50/t)$ . With the above, H. calcs. tables for conversion of time Saybolt Furol to Universal and Redwood Admiralty. EUGENE C. BINGHAM

The standardization of commercial viscometers. M. L. SHEELY. *Ind. Eng.*

*Chem.* 15, 1109-14(1923).—The capillary flow type viscometers have been compared with the MacMichael torsional viscometer for detg. the viscosity of glue. The two types of instruments give results that vary considerably. No explanation is given for the discrepancies.

R. F. SCHNEIDER

Some factors influencing the design of absorption apparatus. R. T. HASLAM, W. P. RYAN AND H. C. WEBER. *Ind. Eng. Chem.* 15, 1105-8(1923).—The "gas film" and "liquid film" are the 2 principal resistances in absorption app. The "gas film" is proportional to the gas velocity to the 0.8 power. The "liquid film" is independent of the gas velocity. The coeff. of absorption rises rapidly with an increase in gas velocity but reaches an asymptote owing to the "liquid film" resistance.

R. F. SCHNEIDER

Cold end compensation on a pyrometer system. C. B. THWING. *J. Am. Ceram. Soc.* 6, 1062-8(1923).—The various methods are described.

C. H. KERR

A thermopile for measuring radiation. W. J. H. MOLL. *Proc. Phys. Soc. London* 35, 257-60(1923).—The thermopile is designed to be quick-reading, sensitive, and free from zero-errors. The cold junctions are in contact with metal masses which keep down their temp., and in order that the hot junctions may have small heat capacity the bi-metallic strips composing the thermopile are made of plates of constantan and manganese Ag-soldered along an edge, rolled in a direction parallel to the edge into thin foil, and then cut into strips perpendicular to the edge.

C. C. VAN VOORHIS

How silica protection tubes cause contamination of thermocouples. O. A. HOUGEN AND B. L. MILLER. *Chem. Met. Eng.* 29, 662-3(1923).—Somewhere between 900° and 1000° vitrified silica tubes become porous through devitrification, causing contamination in a reducing atm., presumably from reduced Si. In 50 hrs. at 1000° a Pt thermal had its e. m. f. lowered  $\frac{3}{4}\%$ , a chromel thermal 4%. At 1200°, a higher temp., the chromel thermal was lowered less, or to 3%. Subsequent heating at 1000° and over in an oxidizing atm. tended to restore the e. m. f. of the Pt thermal. It not only restored the chromel, but carried it above its initial value. [Apparently the reducing contamination renders the chromel more susceptible to change by oxidation than it was originally.]

W. P. WHITE

A new centrifugal for separating solids from liquids. C. R. PLATZMANN. *Chem.-Ztg.* 47, 167-8(1923).—A description, with 5 cuts, of the app. of the Centrifugal Separators, Ltd., London, which combines features of the centrifugal and filter-press. The advantages of the app. are: low 1st cost, low operating cost, can handle suspensions for which presses are not suitable, independent of temps., small floor space, and the sepn. of the solids according to size of grain.

J. H. MOORE

Industrial drying. The apparatus and how it works (BUCK) 13.

Centrifugal apparatus for separating and filtering liquids. C. F. PAUL, JR. U. S. 1,468,740, Sept. 25.

Drainage plates for filters. F. W. MANNING. U. S. 1,470,463, Oct. 9. Structural features.

Apparatus for filtering sugar solutions or other liquids. J. C. SILVESTER. U. S. 1,469,026, Sept. 25.

Evaporator. T. M. SKINNER, JR. U. S. 1,468,679, Sept. 25. Heated liquid is led from a boiler to the first of a series of evaporators and thence from one evaporator to another. A connection leads from the upper portion of the boiler to the last of the series of evaporators and a pump in this connection draws vapors from the boiler and introduces them under increased pressure into the last evaporator. A pump is also provided for taking vapors under suction from the last evaporator and introducing them under increased pressure to the first evaporator.

Plate column apparatus for fractional distillation of alcohol or other liquids. E. A. R. CHENARD. U. S. 1,468,899, Sept. 25.

Apparatus for chilling of liquid edible fatty substances. J. T. COX. U. S. 1,469,896, Oct. 9. Blades on a rotary shaft remove fatty material from the inner surface of a treating cylinder and incorporate it with gas within the cylinder. A jacket is provided on the cylinder for refrigerating its contents.

Glass receptacle for transporting and dispensing neon or other rare gases. P. E. HAYNES. U. S. 1,469,756, Oct. 2.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE I. CLARK

Sir James Dewar. JAMES CRICHTON BROWN. *Science Progress* 18, 126-33 (1923).—Obituary notice with portrait.

To the memory of Johann Wolfgang Doebereiner (1780-1849). F. HENRICH. *Z. anorg. Chem.* 36, 482-4 (1923).

Some chemists of Islam. E. J. HOLMYARD. *Science Progress* 18, 66-75 (1923).—A discussion of the theories and the knowledge of chemistry possessed by Geber, Rhazes, Al-Majriti, and later Muslim chemists, and a description of certain forms of app. used by them.

A critical examination of Berthelot's work upon Arabic chemistry. E. J. HOLMYARD. *Chemistry & Industry* 42, 958-63, 976-80 (1923).

Recent advances in science. Physical chemistry. W. E. GARNER. *Science Progress* 18, 14-8 (1923).—Review of recent work on the constitution of ampholytes.

Chemistry in France in the seventeenth and eighteenth centuries. C. A. SILVERRAD. *Chemistry & Industry* 42, 924-4 (1923).

The emerald table. E. J. HOLMYARD. *Nature* 112, 525-6 (1923).—Of historical interest to chemists.

Recent progress in chemistry. H. LEVINSTEIN. *Chem. Age (London)* 9, 392-3 (1923).—An address.

Correlation of high school and college chemistry. Preliminary report of the Committee on Chemical Education of the American Chemical Society. N. E. GORDON, et al. *Ind. Eng. Chem.* 15, 1189-91 (1923).

Some properties of atoms and electrons as measured by students. FREDERICK PALMER, JR. *J. Optical Soc. Am.* 7, 873-87 (1923).—A plea is made for the use of expts. designed to employ methods as a means to an end rather than to constitute the methods the end in themselves. Three expts., usually considered too elaborate or difficult, are described in detail as being entirely possible for students: (1) the no. of mols. per cc. of gas and the mass of an atom (gas and Cu voltimeters); (2) ratio of charge to mass of an electron (Kaufmann method); (3) electronic charge  $e$  (modified and simplified form of Millikan's oil-drop app.).

The nature of chemical valence. W. NERNST. *Z. anorg. Chem.* 36, 153-5 (1923).—A general consideration.

Electron valency theories and stereochemistry. SAMUEL SUGDEN. *J. Chem. Soc.* 123, 1861-5 (1923).—A criticism of various electronic theories of valency as failing to explain (1) free rotation, and (2) geometrical isomerism.

Theory of free rotation. T. M. LOWRY. *J. Chem. Soc.* 123, 1866-7 (1923).—An answer to Sugden (see above).

The curves of the periodic law. II. W. M. THORNTON. *Phil. Mag.* 46, 442-8; cf. *C. A.* 11, 3135.—A consideration of the relations of d. and at. wt. of the elements by the means of theoretical smooth harmonic curves which are regarded as the components making up the exptl. periodic curves. It is hoped to draw some conclusions as to at. formation from such speculations.

A revision of the atomic weight of boron. The analysis of boron trichloride and boron tribromide. G. P. BAXTER AND A. F. SCOTT. *Proc. Am. Acad. Arts Sci.* 59, 21-48 (1923).— $\text{BCl}_3$  was prepd. in 2 ways, from materials purified by the usual methods of extreme accuracy used at Harvard. (1) B suboxide was heated in a current of dry  $\text{Cl}_2$  and the  $\text{BCl}_3$  formed condensed in receiving bulbs which were subsequently exhausted and sealed.  $\text{Cl}_2$  was removed by shaking with Hg. Other impurities such as  $\text{BBr}_3$ ,  $\text{HCl}$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$  were removed by 20 fractional distns. Further distns. with Hempel columns were made till  $\text{SiCl}_4$  was present in amts. that would affect the at. wt. of B less than 0.007 unit. (2) B which had been completely reduced with Mg and extd. with HCl was allowed to react with dry  $\text{Cl}_2$  as in (1). Subsequent operations were similar to those in (1).  $\text{BBr}_3$  was prepd. by passing He satd. with  $\text{Br}_2$  vapor over B which had been extd. with HBr. Subsequent purification was as in (1) under  $\text{BCl}_3$ . In the analyses a weighed bulb contg. the B halide was broken in  $\text{NH}_3$  soln. and the glass fragments were collected and weighed. The halogen acid liberated by hydrolysis was titrated with  $\text{AgNO}_3$  soln., with the precautions developed by long experience in this type of analysis.  $\text{BBr}_3$  reacted very violently with the  $\text{NH}_3$  soln. and several flasks were broken by the pressure produced. This behavior was not noticed in the chloride. The

results on  $\text{BCl}_3$  and  $\text{BBr}_3$  agree well as to the at. wt. of B and the final value given is  $B = 10.820$  ( $A_g = 107.880$ ).

**The crystal structure of strontium selenide.** MABEL K. SLATTERY. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 84(1922).— $\text{SrSe}$  has a simple cubic lattice with  $d = 3.10 \text{ \AA}$ . The unit cube has a side  $3.10 \text{ \AA}$ , alternate corners being occupied by Sr and Se atoms.

**Crystal structure of vanadium, germanium and graphite.** A. W. HULL. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 113(1922).—V has a body-centered cubic lattice, side  $3.04 \text{ \AA}$ ; distance between nearest atoms,  $2.63 \text{ \AA}$ ; ideal  $d$ ,  $5.76$ . Ge has the same structure as the diamond. The side of the unit cube is  $5.63 \text{ \AA}$ ; distance between nearest atoms,  $1.218 \text{ \AA}$ ;  $d$ ,  $5.36$ . Graphite shows a lattice of the hexagonal close packed type, which is not in agreement with results of Debye.

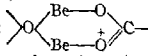
**Effect of occluded hydrogen on the crystalline space lattice of palladium.** L. W. MCKEEHAN. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 82(1922); cf. C. A. 17, 2068.—Preliminary expts. show that the effect of occlusion of H is to increase by several per cent the parameters of the face-centered cubic lattice of Pd without altering its form.

**Lattice determinations by means of the line-shift relation (Schichtlinienbeziehung).** H. MARK, K. WEISSENBERG AND H. W. GONELL. *Z. Elektrochem.* 29, 364-5(1923).—A lecture.

**Stereochemistry of crystallized substances.** WILHELM BILTZ. *Z. Elektrochem.* 29, 348-54(1923).—An address.

**X-rays and crystal symmetry.** T. V. BARKER. *Nature* 112, 502-5(1923); cf. C. A. 17, 2375, 3117.—B. takes strong exception to the statement by Wyckoff, that, because in such cases as  $\text{NH}_4\text{Cl}$  different symmetries are revealed by X-rays and by crystallographic measurements, the latter should be dismissed as untrustworthy. Citing the work of Pasteur, B. shows that surface studies lead to a real knowledge of crystal symmetry, provided they are interpreted by the principle of the greatest common measure. Any higher symmetries are pseudo-symmetries, and have their origin in the suppression of certain determinants. A notable example is X-ray symmetry, for it is compulsorily based on an at. conception of cryst. structure and not on the mol. basis demanded by a wealth of chem. facts. An attempt is made to bridge the gulf between X-ray symmetry and crystal symmetry, but it is felt that "the real solution is not yet in sight because of the lack of a general chem. method of investigating crystal structure *in situ*."

**The structure of basic beryllium acetate.** N. V. SIDGWICK. *Nature* 111, 808-9(1923).—The attempt is made to give the compd.  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ , a formula in accordance with its properties, including the crystal structure given by Bragg (C. A. 17, 2208). At the center an O atom is attached to 4 Be atoms. The octet of O is made up of 4 electrons from the 4 Be atoms and 4 from the O, which must lose 2. The attachment

of acetate group to 2 Be atoms is as follows:  In forming

the ring each acetate group must lose an electron from the carbonyl O, so that the 6 give up 6 electrons, in addition to the 2 from O. Thus 2 electrons go to each of the Be atoms, increasing its valency electrons from 2 to 4, enabling it to form 4 non-polar links, 1 to O and 3 through acetate groups to each of the other 3 Be atoms.

**The crystalline structure of anhydrous racemic acid.** W. T. ASTBURY. *Proc. Roy. Soc. (London)* 104A, 219-35(1923).—A continuation of the study begun with tartaric acid (C. A. 17, 1740). From X-ray spectrometer data the unit cell is associated with 1 mol.  $\text{C}_4\text{H}_4\text{O}_6$  but is not the true fundamental cell (triclinic pinacoidal). The latter is associated with 1 mol. of right-handed and 1 mol. of left-handed tartaric acid. There is no evidence that racemic acid exists as an independent inactive doublet of mol. wt. 300. The chem. mol. is substantially of the same shape and dimensions as the mol. in tartaric acid. A small contraction (7.69 to 7.41  $\text{\AA}$  on a axis) and the absence of a certain cleavage is associated with small changes in phys. properties which accompany the formation of racemic acid from its active components. The disappearance of the distortion of the hydroxyl groups of tartaric acid is favorable to the theory of anomalous optical properties of the active acid. An explanation is given of the multiple twinning and irregular growth of anhydrous racemic acid.

**Comments on a communication by Astbury.** WALLERANT. *Compt. rend.* 176, 1518-9(1923).—Astbury, using the methods of the Braggs, has detd. the cryst. structure of tartaric acid and has found that the 4 central C atoms lie at the corners of an irregular tetrahedron. (Cf. C. A. 17, 1740.) This causes the dissymmetry indicated by the

stereoisomeric properties, and confirms a prediction of Pasteur's made in 1860.

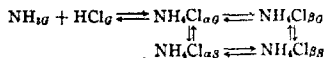
S. K. ALLISON

**The compressibility of hydrogen at high pressures.** P. W. BRIDGMAN. *Rec. trav. chim.* **42**, 568-71(1923).—The detn. of the compressibility of  $H_2$  compared with other gases offers peculiar difficulties. B. first tried compressing the  $H_2$  directly inside a large steel cylinder. This method failed because of the penetration of the steel by the  $H_2$ . At room temps. and 9000 kg. pressure  $H_2$  is forced through the walls of any steel container with which it is in direct contact. "The  $H_2$  is apparently absorbed by the steel which is thereby weakened. Some local irregularity detrs. the place of most rapid attack; the action once started is cumulative so that the  $H_2$  escapes along a radial fissure with explosive violence, leaving behind it an open seam." The entire action occurs in a few secs. The vol. of  $H_2$  under 13,000 kg. is so small that the mean distance between the centers of mols., simple cubic arrangement being assumed, is  $2.9 \times 10^{-8}$  cm., a close approach to the dimensions of the mol. computed from the kinetic theory. The d. of  $H_2$  at 13,000 kg. and  $30^\circ$  is 0.137, 1.8 times the d. of solid  $H_2$  at the triple pt. "It is of interest to inquire whether the behavior of  $H_2$  at high pressures is what would be expected from that at low pressures, or whether there are new tendencies called into play by the high pressure. In the first place the ordinary van der Waals equation, the consts. being computed from the crit. data, gives impossible results, for at 13,000 kg. the vol. of  $H_2$  is less than 'b' of the equation. This is what might be expected, and indicates that the mol. is itself compressed at these high pressures, as does also the much greater d. of the high pressure gas compared with the low pressure solid." For the details of manipulation and the numerical data see the original. E. J. W.

**Coefficients of viscosity and slip of carbon dioxide by the oil drop method, and the law of motion of an oil drop in carbon dioxide, oxygen and helium, at low pressures.** J. M. EGLIN. *Phys. Rev.* **22**, 161-70(1923).—The coeff. of viscosity for  $CO_2$  at  $23^\circ$  and 76 cm. pressure was found to be  $1.478 \times 10^{-4}$ , in good agreement with the value  $1.472 \times 10^{-4}$  obtained by the const. deflection method by Van Dyke. The const.  $A$  in the modified Stokes' law came out 0.815. Measurements of the motion of oil droplets in  $CO_2$ ,  $O_2$  and He were extended to pressures of 1.9, 2.0 and 10 mm. resp., and to values of  $l/a$ , the ratio of mean free path to oil drop ratio, of 76, 130 and 71, resp. The empirical correction factor to Stokes' law,  $f(l/a) = 1 + (l/a)(A + B e^{-Cn/l})$ , was found to hold for all, the values of  $(A + B)$  being the same for all and equal to 1.175. A new atomizer for use at low pressures was developed. The formulas of Leonard and Langevin for large ions are both the same as the empirical law for droplets, but the Wellisch formula cannot be extended to droplets whose mass is large with respect to the mass of the mol. A. E. STEARN

**The purification of neon and a new determination of the critical temperature of neon.** C. A. CROMMELIN. *Rec. trav. chim.* **42**, 814-7(1923).—The prepn. of pure Ne by fractionation of a mixt. of gases contg. 30% Ne is briefly described. The pure product was used in detg. the isotherms, vapor tension, crit. point, etc., of Ne. This same Ne was further fractionated for the detn. of the d. curve and the diameter of Ne in an app. that is illustrated and described. E. J. WITZEMANN

**The ammonium chloride problem.** A. SMITS. *Rec. trav. chim.* **42**, 826-9(1923).—No plausible explanation exists of the fact that moist  $NH_4Cl$  vapor is almost completely dissociated into  $NH_3 + HCl$  while intensively dried non-dissociating  $NH_4Cl$  has almost the same vapor tension. S. has proposed a hypothetical explanation based on his theory of allotropy. Investigation has shown that  $NH_3$  consists of various types of mols. and S. assumes that 1 of these types is chemically inactive. He assumes only 2 types of  $NH_4Cl$  mols., one of which,  $NH_4Cl_\alpha$ , dissociates and the other,  $NH_4Cl_\beta$ , does not but is more volatile. The heterogeneous equil. between solid and gaseous  $NH_4Cl$  in the moist state can then be represented as follows:



S. further supposes that by intensive drying the inner equil. is displaced towards the side of the inactive  $\beta$ -pseudo component and indeed practically totally so in both co-existing phases. The gaseous phase will then, like the solid phase, contain practically only the  $NH_4Cl_\beta$  type of mol. and it is clear  $(NH_4Cl_{\alpha g})_{dry} > (NH_4Cl_{\alpha g})_{moist}$ , is possible. In fact, if the vapor pressure of the pseudo-component  $NH_4Cl_\beta$  is several times as great as that of the pseudo-component  $NH_4Cl_\alpha$  it would then be possible that  $(NH_4Cl_{\beta g})_{dry} > [(NH_4Cl_{\alpha g}) + (NH_{3g}) + (HCl_g)]_{moist}$ . The results of A. Smith and Lom-

hard (C. A. 9, 748) on HgCl are discussed similarly and it is suggested that HgCl and NH<sub>4</sub>Cl belong to 2 oppositely situated types of pseudo-systems. E. J. W.

The second virial coefficient of gases. ANGUS F. CORE. *Phil. Mag.* 46, 256-72(1923). S. C. L.

The properties of fluids in the state of saturation near the critical point. J. E. VERSCHAFFELT. *J. phys. radium* 4, 158-69(1923); cf. Bruhat, C. A. 17, 1909.—Mathematical. The method consists in expressing the pressure in series in terms of  $(v - v_c)$  and  $(T - T_c)$  near the crit. point and applying the principles of thermodynamics to this equation of state near the crit. point. The method is applied to a particular equation of state chosen as a result of a study of the direction of isotherms and of the curve of satn. This equation indicates that each isotherm at a detd. point has an analytical discontinuity which observed results near the crit. point seem to confirm. This discontinuity in the direction of the isotherms is not in disagreement with the phys. continuity of the liquid and gaseous states, which require that all the states of homogeneous fluids can be represented by one characteristic equation.

H. M. McLAUGHLIN  
New proof of the specular reflection of molecules. R. A. MILLIKAN AND K. S. VAN DYKE. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 95(1922); cf. Millikan, *Phys. Rev.* 21, 217-38; Stacy, *Ibid* 239-49; Van Dyke, *Ibid* 250-65.—Measurements of the coeff. of slip by the const. deflection method using concentric cylinders confirm the results on specular reflection of mols. previously obtained by the oil-drop method.

S. K. ALLISON  
Note on the chemical constants of diatomic gases. J. R. PARTINGTON. *Phil. Mag.* 46, 329-30(1923); cf. C. A. 17, 600.—A comment on an equation of Sackur as compared with that of P. for the chem. const. of diat. gases. S. C. L.

Vapor pressure of monatomic elements. R. W. MILLAR. *J. Am. Chem. Soc.* 45, 2323-9(1923).—The differential equation,  $d\mu/dt = \Delta H/T\Delta V$  for vapor pressures becomes  $d \log p/d \log t = \Delta S/R$  when the vol. of liquid is neglected and when the vapor is assumed to obey the gas law. The value of  $\Delta S$ , the change in entropy, is  $\int_{T_0}^T C_p d \log T$ . Also  $C_p = \alpha + \beta \log T$  accords with the facts over fairly large temp. ranges. Using these formulas an integral form is found for  $p$ , the vapor pressure of the liquid, as a function of temp. This equation agrees well with the known values for Hg, Na, Zn and H over wide temp. ranges.

JAMES M. BELL  
Calculation of the molecular weight of associated and non-associated liquids from critical data. W. HERZ. *Z. Elektrochem.* 29, 394-5(1923).—Berthelot's formula, with non-associated liquids, gives fairly correct mol. wts. at low temps. and very exact results at high temps. With associated liquids, the calcd. mol. wts. are too high at low temps., but fairly accurate at very high temps.

H. JERMAIN CREIGHTON  
The wetting of glasses by mercury. E. E. SCHUMACHER. *J. Am. Chem. Soc.* 45, 2255-61(1923).—A considerable number of expts. were made to det. the extent to which Hg wets quartz and different glasses after absorbed gases are removed by heating to at least 400° for 2 days at a pressure of  $10^{-6}$  mm. Under such conditions, quartz is wetted by Hg, Pyrex glass is occasionally wetted, but soda glass very seldom. It appears that the more alk. a glass is the less readily it is wetted; and it is suggested this is due to a surface film of hydrolysis products, NaOH and SiO<sub>2</sub>, which may perhaps also retain gases.

A. W. HENNEY  
Radial flow in rotating liquids. HAROLD MOTTSMITH AND IRVING LANGMUIR. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 95(1922).—M. and L. offer an explanation of the appearance of colloidal sols. of V<sub>2</sub>O<sub>5</sub> which are rotated in a beaker and examd. in polarized light. The bottom of the rotating column is retarded by the viscous drag of the bottom of the beaker, and the unrestricted rotation of the top causes an unbalanced centrifugal force with resulting radial flow.

S. K. ALLISON  
An investigation of the angle of contact between paraffin wax and water. R. ABLETT. *Phil. Mag.* 46, 244-56(1923).—A new method of measuring the angle of contact ( $\theta$ ) consists in detg. the depth ( $h$ ) to which a cylinder of diameter ( $d$ ) coated with paraffin wax must be immersed in water to cause the free liquid surface to become plane right up to the line of contact with the curved cylinder. The levels were read by means of light reflected from the lower water surface. The formula used is  $\cos \theta = (2(h/d) - 1)$ . Measurements were also made with the paraffin cylinders in rotation. When the paraffin surface is moving away from the water surface, a condition of wetting is produced, and *vice versa*. The results obtained are  $\theta = 104^\circ 34' \pm 5'$ ;  $\theta_1 = 113^\circ 9' \pm 5'$ ;  $\theta_2 = 96^\circ 20' \pm 5'$ . From the fact that  $\theta_1$  is greater than  $\theta_2$  it follows that the surface energy of the air-solid interface has been increased by having been in contact with

the liquid. From this it is concluded that the solid has adsorbed some of the liquid. This explains the difference in the heights of liquid in a capillary tube with rising and falling meniscus, also the difference in thickness of expanding or contracting drops of the same size. It is further apparent that the degree of wetting depends on the range ( $\theta_2 - \theta_1$ ) or the degree to which the surface energy of the solid is affected by contact with the liquid. Wetting is therefore possible for obtuse as well as acute angles of contact.

S. C. LIND

**Surface tension at the boundaries of crystal grains in crystals.** C. H. DRESCHE. *Rec. trav. chim.* **42**, 822-5 (1923).—Quincke (*Ber. physik. Ges.* **5**, 102 (1903)) suggested that in the solidification of a liquid a preliminary sepn. into 2 immiscible liquid phases takes place, 1 of those phases behaving towards the other like oil in  $H_2O$ . A foam would thus be formed (Q., *C. A.* **7**, 761). The form of crystal grains was studied (Dresch, *C. A.* **13**, 3143). In this paper the results on the form of crystal grains in (a) soap, resin and gelatin foam cells, (b) crystal grains of  $\beta$ -brass, and (c) crystal grains of chrome steel, are brought together in 1 diagram, which shows that there is a close correspondence between the form of the cells in a foam and that of the crystal grains in a metal. It does not follow that Q.'s hypothesis is true, but the results show that surface tension, which det. the form of foam cells, is also concerned in the production of the grain boundaries in metals.

H. J. WITZEMANN

**Solid solutions.** WALTER ROSENTHAL. *Trans. Am. Inst. Mining Met. Eng.* **1923**, No. 1250-N, 32 pp.—A phys. conception of the mechanism of the formation of solid solns. is presented, rather than a thermodynamic treatment. The assumption is made that solid soln. crystals contain internally stored energy and that it is the amt. of this stored energy which det. the limits of solid soly. in these bodies. A simple crystal is conceived to be built up of atoms fixed upon an imaginary framework in space. The fundamental theory is adopted that in a crystal of a solid soln. alloy, the solute atoms are placed upon the actual lattice of the solvent metal in simple substitution for the atoms of the solvent. Such a substitution causes a distortion of the lattice which is both "local" and "general," in relative amts. varying as the lattice is flexible or stiff. Based upon such a conception, several inferences follow in a logical and direct manner. (1) The amt. of energy stored in the composite lattice det. the limit of solid soly., and the amt. of this energy is dependent on the amt. of distortion which the introduction of the solute atom produces. (2) A distorted lattice implies an increased degree of hardness and strength and a diminished degree of ductility. (3) Because of the stored energy within a distorted lattice, less heat need be applied to bring about transition to the liquid phase, i. e., the m. p. is lowered. Local distortion governs the position of the solidus, while general extension governs the position of the liquidus. These 3 considerations connect strength and hardness with high m. p. and with the tendency to form long ranges of solid solns., a connection which suggests the possibility of quant. calens. as soon as the at. const. involved become known. (4) The phenomenon of diffusion can be accounted for by conceiving slip to occur, one at. step at a time, toward the regions of low concns. of solute atoms in the lattice. (5) The fact that in many ternary alloy systems, the introduction of one metal seriously diminishes the soly. of the other, finds explanation in this theory since, if the distortion caused by the 2 kinds of solute atoms is in the same direction, each kind of solute atom will mutually tend to diminish the soly. of the other. (6) While a solid soln. crystal cannot be regarded as having anything but a single lattice, an intermetallic compd., on the other hand, is supposed to possess 2 or more interpenetrating lattices. This furnishes an explanation for the brittleness of such compds., since the resistance to slip (i. e., the brittleness) increases with the complexity of the lattice. Finally, some of the factors affecting the phenomena of increased soly. with increased temp. are pointed out, but a complete explanation is avoided because of the meagerness of the data available.

E. A. MEAD

**The partial decomposition of certain solid substances effected by grinding.** JOHN JOHNSTON. *Rec. trav. chim.* **42**, 850-4 (1923).—The process of grinding a solid may be accompanied by certain changes in the compn. of the material. In particular it may cause a solid substance, which on dissociating yields a gaseous product, to lose some part of this volatile component. From theoretical considerations it appears that this partial loss of volatile component may occur more generally than has hitherto been supposed; and expt. has confirmed this deduction. In many cases the loss will be inappreciable because the dissoc. pressure is too small or the rate of dissoc. too small, or because the substance is not hard and crushes easily. In other cases like the hydrates the loss may be so large as seriously to affect analytical results.

H. J. WITZEMANN

**The diffusion coefficient in solids and its temperature coefficient.** SAUL DUSH-



MAN AND IRVING LANGMUIR. *Proc. Am. Phys. Soc.* **1922**, *Phys. Rev.* **20**, 113(1922).—Equations are given by which the temp. coeff. of the diffusion coeff. of solids in solids can be calc. from the value of the diffusion coeff. at any one temp. Examples are given for the diffusion of Th through W.

S. K. ALLISON

**Adsorption and the corresponding states.** RICHARD LORENZ AND A. LANDE. *Z. anorg. allgem. Chem.* **125**, 47-58(1922).—A theoretical paper in which the conclusions of Bucken (*C. A.* **8**, 3390; **16**, 1525) are discussed. The present authors claim that adsorption phenomena can be employed to calc. the dipolar moment of the adsorbed mols. They explain the apparent independence of the adsorption potential of the temp. by assuming that the bulk of the adsorbed substance is concd. on the adsorbing surface and that the orientating tendency of the adsorption force is much greater than the kinetic force produced by a higher temp. In the regions where Henry's law is obeyed, it is shown that the amt. of gas adsorbed divided by its crit. temp. is the same for all gases except H<sub>2</sub>. The const. is equal to about 13; this is a strong argument for the identity of adsorption and mol. cohesion forces.

J. C. S.

**Negative adsorption. III. Action of gelatin on aqueous solution of sodium chloride, etc.** M. A. RAKUZIN AND T. GENKE. *Biochem. Z.* **137**, 341-6(1922); cf. *C. A.* **17**, 1570.—Gelatin swells in NaCl solns. of various concns. and in other solns. by taking up all components of the soln. Gelatin dissolves in satd. NH<sub>4</sub>Cl and satd. BaCl<sub>2</sub>. **IV. Action of gelatin on some acids.** *Ibid* 347-8.—In certain org. and inorg. acid solns. the acid concn. is diminished after swelling; a gelatin salt has been formed. **V. Action of agar-agar on ammonium chloride.** M. A. RAKUZIN. *Ibid* 349-52.—The agar takes up some of the soln. These instances are taken as evidence that in the swelling of gelatin, etc., negative adsorption in the sense of Ludwig is not a factor. **VI. Action of gelatin on aqueous solutions of ethyl alcohol.** M. A. RAKUZIN AND T. GENKE. *Ibid* 353-5.—In strong EtOH solns. (sp. gr. up to 0.875) no change occurs. From more dil. solns. (sp. gr. to 0.97) gelatin takes up the soln. Air-dried gelatin loses H<sub>2</sub>O in EtOH soln. of sp. gr. 0.981.

GEORGE ERIC SIMPSON

**The stereometry of dispersoids.** WA. OSTWALD. *Kolloid-Z.* **32**, 77-80(1923).—There are 4 fundamental stereometric conditions, independent of the chem. nature or state of aggregation of the materials involved, for the appearance of colloidal properties, of which the first is necessary and sufficient and the others of a descriptive nature: (a) the absolute size of at least one dimension of the particles, (b) the relative volume proportions of the 2 or more phases in question, (c) the kind of interfacial configuration (particles, threads, or strata), (d) whether the colloidal surface development takes place for one or both (or more) phases. The conception of specific surface has not seemed suitable for describing the characteristics of the colloid state and its reciprocal, the continuity has been substituted. The ratio of the total vol. of the system to the interfacial area is the *total continuity*,  $K_t$ . The ratio of vol. of dispersed phase to interfacial area is the *partial continuity*,  $K_p$ , and is a measure of the degree of dispersity. For spherical particles  $K_t = \pi d^3/\pi d^2 = d/6$  where  $d$  is the particle radius. For threads  $K_t = d/4$  and for films  $K_t = d/2$ . The ratio of vol. of dispersion medium to interfacial surface is *partial continuity*  $K_m$ . From the definitions it follows that  $K_t = K_p + K_m$ . Colloidal phenomena appear when either  $K_t$  or  $K_p$  or both lie between  $1/60 \mu$  and  $1/6 \mu$  for three dimensional colloids (particles or droplets),  $1/40 \mu$  and  $1/4 \mu$  for two dimensional colloids (threads), and  $1/20 \mu$  and  $1/2 \mu$  for one dimensional colloids (films). For simple colloids such as dil. sols, milk, smoke, mist  $K_t$  is of colloidal dimensions but  $K_p$  and  $K_m$  are not. There is a transitional case of no particular significance where both  $K_t$  and  $K_p$  are of colloidal size but  $K_m$  is not. When all three are of colloidal dimensions one has a *double colloid*. Most coagulation products of colloids belong to this class. When the vol. ratio of 1 of the phases is less than 30% only simple colloidal systems are possible; when it is between 30% and 70% double colloids may be formed. These considerations are independent of the degree of dispersion and hold for coarse suspensions and true sols. as well as for colloids.

F. L. BROWNE

**Studies of the dispersoid synthesis of gold. I.** P. P. VON VEIMARN. *Kolloid-Z.* **33**, 74-81(1923).—Necessary conditions for the prepn. of stable Au sols by reduction with HCHO are (1) the insoly. of Au in H<sub>2</sub>O, (2) the great rapidity of the reaction and of the sepn. of the solid phase, and (3) maintenance of sufficiently low concns. of the reacting solns. to avoid coagulation by the by-products. If the Au is obtained first as a colloiddally dispersed compd. such as Au(OH)<sub>3</sub>, the reduction need not take place rapidly. Au(OH)<sub>3</sub> is dispersed by Au salts or alkalis. When a "disperser" is present the concns. of reacting solns. may be considerably higher. The action of alkalis on HCHO may result in the formation of HCOOH and CH<sub>3</sub>OH, in polymerization, and in the formation of formose. The latter on heating gives a yellow to brown soln. which

contains colloiddally dispersed material, "H dispersoid." The "H-dispersoid" plays an important part in stabilizing the Au sols. Au sols were prepd. from com. reagents as follows: To 500 cc. of  $H_2O$  at room temp. were added successively (a) 10 cc. of a soln. of 1 g.  $AuCl_3 \cdot HCl \cdot 4H_2O$  per l., and (b) 10 cc. of a mixt. of 1 cc.  $HCHO$  soln. and 9 cc. 0.2 N  $KOH$ . Red sols of amicroscopic particles resulted. These were unstable and coagulated in 48 hours. If the water was boiled before addn. of the reactants and boiling continued for various lengths of time up to 70 min. the stability of the sol increased with the time of boiling, becoming permanently stable after 60 min. The increased stability of the Au sol is due to the "H-dispersoid." On dissolving the Au of the stable sols by addn. of  $KCN$  the same yellow-brown color was obtained as when the  $HCHO$  and  $KOH$  mixt. is boiled in water without addn. of the  $AuCl_3$ . In these expts. the  $KOH$  may be replaced with  $K_2CO_3$ .

F. L. BROWNE

**Note concerning the dispersoid synthesis of silver and of mercury by the formaldehyde method.** P. P. VON VEMARN. *Kolloid-Z.* **33**, 81, 2 (1923).—Ag sols can be made by the method of the preceding abstr. by using 0.001 N  $AgNO_3$  soln. in place of the  $AuCl_3$  soln. When  $HgNO_3$  soln. is employed the Hg sol is contaminated with  $Hg_2O$ . On prolonged boiling of the Hg sols the Hg goes back into soln.

F. L. BROWNE

**Contribution to general colloid chemistry. VII. The analysis and constitution of colloidal silver.** I. PAUL NEUREITER AND W. PAULI. *Kolloid-Z.* **33**, 67-73 (1923).—The colloidal Ag sols were prepd. by dissolving freshly pptd. and washed  $AgCl$  in 20%  $NH_3$ , diluting, and reducing with  $N_2H_4OH$ . The sols were red in transmitted light, greenish gray and opalescent by reflected light. The sols remain unchanged for months when kept in stoppered flasks. Chlorides ppt.  $AgCl$  from these sols and heavy metal salts give a ppt. contaminated with the metal hydroxide. An ammoniacal soln. of  $ZnSO_4$  makes a good pptg. agent. The Ag pptd. from the sols was thoroughly washed, dried to const. wt. at  $100^\circ$  and then analyzed for  $O_2$  by heating in a stream of  $CO_2$  and measuring the  $O_2$  evolved. Two g. of the Ag contained 0.02 cc.  $O_2$ , a negligible amt. The ppt., which had been dried to const. wt. at  $100^\circ$ , on further heating lost 0.0197 g.  $H_2O$ , about 1 mol.  $H_2O$  to 18 atoms of Ag. On prolonged dialysis the elec. cond. finally became approx. const. at values ranging from  $6.10 \times 10^{-8}$  to  $21.10 \times 10^{-8}$  reciprocal ohms for different sols. The different end values are attributed to differences in the constitution of the sols. The dialyzed sols are stable when kept in tightly stoppered flasks. On dissolving the sols in  $HNO_3$  a small amt. of  $AgCl$  was left behind. The coagulating powers of various electrolytes were found to be in the order  $KNO_3 < AgNO_3 < Ba(NO_3)_2 < Hg(NO_3)_2 < HgCl_2 < Hg(NO_3)_2 = H_2SO_4$ . Pure serum albumin exerts a coagulating effect on the sols. The constitution of the sols is considered to be  $[xAg \cdot yAgCl \cdot AgCl] Ag^- (NH_3)_z^+$  in which the part in brackets is the negatively charged colloid particle and the rest the corresponding cation.

F. L. BROWNE

**Low concentrations in colloid chemistry.** H. R. KREYF. *Chem. Werkblad* **18**, 475-9 (1921).—A recapitulation of the present knowledge of the influence of traces of electrolytes on the stability of colloidal sols.

J. C. S.

**Precipitation of sols by alcohol.** W. D. BANCROFT. *Rec. trav. chim.* **42**, 733-5 (1923).—According to Billitzer (*Z. physik. Chem.* **45**, 312 (1903)) Pt is charged negatively in  $H_2O$  and positively in  $EtOH$ , the reversal occurring at about 75%  $EtOH$  by vol. This means that a colloidal soln. of Pt would be pptd. by the addn. of sufficient  $EtOH$ . There seems to be no especial reason why the effect of  $EtOH$  on Pt should be specific and it is therefore concluded that  $EtOH$  tends to ppt. negatively charged sols. The actual pptn. may depend on the presence of salts which bring the colloid nearer to the isoelectric point, thus making the sol less stable. Several similar cases are cited. In discussing this phenomenon it is shown that the effect is due in great part to adsorption of  $EtOH$ . Since sols can also be brought to the isoelectric point by adding suitable electrolytes, this means that the so-called soln. pressure can be changed in this way, i. e., the soln. pressure may change with the solvent. Formulas for c.m.f.s. and soly. changes are deduced on the implicit assumption that there is no adsorption and consequently are in error to some extent. It remains to be seen whether the error is appreciable in most cases. In any case it is quite evident that the orthodox phys. chemistry must be modified so as to take account of effects due to adsorption.

E. J. WITZEMANN

**Myricyl alcohol "jellies."** E. H. BUCHNER. *Rec. trav. chim.* **42**, 787-9 (1923).—Fischer and Bobertag (*Jahresber. Schles. Ges. Vaterl. Kultur* **86**, 33 (1903); cf. *C. A.* **3**, 2265) considered that their observations on "jellies" obtained from myricylate (*A*) in org. solvents supported the idea that these systems consist of 2 liquid phases. B. has repeated their expts. using the same solvents ( $CHCl_3$  and amyl alc.). The results show that the soly. curves after rising quickly to about  $40^\circ$  and  $60^\circ$ , resp., run at once in the direction of the m. p. of *A* ( $86^\circ$ ). They have a nearly uniform slope and do not show anything like a horizontal part (a zone of demixtion). This proves that *A* is completely

miscible in the liquid state with  $\text{CHCl}_3$  and amyl alc. Consequently the evidence in favor of the emulsion theory of jelly structure is lost. The expts. show this jelly to be a conglomerate of very fine crystals which retain a large amt. of liquid in the meshes. The solid particles can be seen disappearing and reappearing. There seems to be no doubt about the structural elements of these jellies, but it is another question, whether the above conclusions may be generalized for all jellies, *e. g.*, of gelatin. The word jelly has no well defined meaning and widely different things are comprised within this conception. B. proposes to retain the name jelly (Gallerte) only for the systems of gelatin and like substances which have been thus named of old. E. J. WITZEMANN

**A study in rhythmic series of chemical changes.** K. C. VIRARACHAVA. *Chem. News* 126, 289-91(1923).—A summary of present knowledge of rhythmical reactions, particularly the Liesegang phenomenon. In expts. by V., rings appeared at intervals in rhythmical order, but after some time, beyond the range of the rings but contiguous to them, several bands in thin films of different colors were deposited continuously. When the concn. of the 2 reagents was approx. equal, the ppt. appeared continuous but under the microscope it was finely banded. When there is a difference in concn. the rings appear, and at the stage when the concns. become equal, the ppt. is formed in a continuous manner. The existence of *quanta* may not be limited to energy and it is possible that reactions may be discontinuous. C. C. DAVIS

**Liesegang rings. III. The effect of light and hydrogen-ion concentration on the formation of colloidal gold in silicic acid gel.** Rhythmic bands of purple of Cassius. E. C. H. DAVIES. *J. Am. Chem. Soc.* 45, 2261-8(1923); cf. *C. A.* 17, 1743.—Light of short wave length catalyzes the formation of colloidal Au in  $\text{SiO}_2$  gel when the expt. is carried out according to the method of Holmes (*C. A.* 12, 2269). The multicolored zones obtained by Holmes were not true Liesegang bands as they were not obtained in the dark but only in changed light. This observation removes Baneroff's objection to Holmes' diffusion theory of Liesegang band formation. The particles of colloidal Au are smaller the lower the H-ion concn. True Liesegang bands of purple of Cassius were prepd. HARRY B. WEISER

**Protective colloids. XIV. Norgine as a protective colloid. I. General colloido-chemical investigation of the extract of norgine.** A. GUTDIER, E. SAUER AND G. KRÖNER. *Kolloid-Z.* 33, 92-8(1923).—Two samples, *D* and *H*, of norgine, the  $\text{NH}_4$  Na salt of laminaric acid, were investigated. *D* contained 12.07%  $\text{H}_2\text{O}$  and 16.45% ash; *H*, 12.62%  $\text{H}_2\text{O}$  and 6.13% ash. A neutral ext. is prepd. by extn. for 4 days with warm water, the ppt. formed being filtered off and the ext. clarified with cellulose (cf. *C. A.* 17, 2800). Solns. of various strengths were prepd. and dialyzed (cf. *C. A.* 16, 3559). Dialysis reduced the % ash and gave a white product. Electrolysis pptd. the colloid at the anode. On standing, ppts. slowly formed in the *D* solns., more rapidly in the *H* solns., accompanied by increase in the ash content of the ext. A decrease in viscosity occurred with age, especially in concd. solns. The stability of the ext. was improved by dialysis. On heating, deep-seated irreversible changes occur, more marked with the higher concns. On cooling, the viscosity does not return to the original value. Acetone and ether cause flocculation, the latter only in high concns.  $\text{CHCl}_3$ , ether and  $\text{AcOMe}$  stabilize and clarify the dil. solns. Abs.  $\text{EtOH}$ , or  $\text{MeOH}$ , produces a stiff gel with systems *D* or *H* of 0.88-0.81% dry substance, a ppt. in *D* and *H* solns. of 0.6%, no ppt. in *D* and *H* solns. of 0.4%, and gives a stabilizing action to solns. of 0.15%. Electrolytes produce gelatinous ppts. which are peptized and stabilized by  $\text{NaOH}$ . C. B. EDWARDS

**Spherical double layers in liquids containing ions.** A. GYEMANT. *Z. Physik* 17, 190-201(1923).—Mathematical discussion. The results are especially applicable to colloid physics. The distribution of potential in such a liquid is expressed by a differential equation which is, in general, not capable of soln. An approx. soln. for certain limiting cases is given. A. E. STEARN

**Sources of error in the measurement of the electric charge of colloidal particles by the method of moving boundaries. Improved method based on a direct measurement of the potential gradient across the boundary.** J. N. MUKHERJEE. *Proc. Roy. Soc. (London)* 103A, 102-21(1923); cf. *C. A.* 16, 3018.—The U-tube method of moving-boundaries for measuring the elec. charge of colloidal particles is unreliable because of non-uniform variation in the resistance of the liquid at different places in the tube. The causes of this variation are (a) electrolysis at the electrodes and diffusion of the products of electrolysis and (b) migration of ions across the boundary. Direct measurement of the p. d. under which the boundary moves, in the colloid, and in the electrolyte just near it, is made by an improved U-tube glass app. It consists of narrow tubes about 4 mm. bore fused to one limb at 4 different positions at distances of about 1 cm.

These 4 side-tubes permit of 3 potential measurements. The p. d. between 1 and 2 gives the av. gradient or the resistance in the electrolyte layer above the boundary, which is just above the fused end of the side-tube 3. The potential drops between 2 and 3 and between 3 and 4 give, resp., the av. gradient across the boundary and in the colloid below the boundary. The boundary is assumed to be between 2 and 3. This improved method makes it possible to follow the changes in resistance that take place during the movement of the boundary. Then the conditions can be detd. which give reliable values of the rate of migration. The method gives results correct within 5%. The velocity of migration of particles of colloidal  $\text{As}_2\text{S}_3$  does not appreciably change with diln. During a period of 21 days the velocity was almost const., though a considerable amt. of  $\text{H}_2\text{S}$  had been formed by the decomn. of the sulfide. I. NEWTON KUGELMASS

**Surface phenomena in sucrose solutions.** R. R. BUTLER. *J. Chem. Soc.* **123**, 2060-5 (1923).—Expressing surface tension ( $\delta$ ) in dynes/cm. the relation between  $\delta$  and  $t$  for sucrose solns. up to 0.82  $N$  is described by the equation:  $\delta = \delta_0(1 - 0.00247 t + 0.0000169 t^2)$ . The equation connecting the surface tension of water with that of a soln. is  $\delta_s = \delta_0 + 2.23y$ , where  $y$  is the mol. concn. From these results it is possible to calc. the deficiency of solute in the surface by the Gibbs equation:  $u = -c^2 RT(\partial\delta/\partial c)$ , where  $c$  is the concn. in g./cc. and  $u$  is the deficiency in g./cm. By using Morse's data (*C. A.* **6**, 2706) for osmotic pressure it is shown that the relationship  $Pu = Kc^2$  holds up to 20% solns. for a limited range of temp. JAMES M. BELL

**A special case of the supposed volume change in solution equilibrium.** BENNY COHEN, WILHELM A. T. DE MEESTER AND A. L. TH. MOESVELD. *Rec. trav. chim.* **42**, 779-83 (1923).—Cf. *C. A.* **17**, 3123. E. J. WITZEMANN

**The conception of acids and bases.** J. N. BRÖNSTED. *Rec. trav. chim.* **42**, 718-28 (1923).—This paper is designed to exhibit the advantages connected with a modified conception of a base. Preliminary discussion is followed by the following definition. Acids and bases are substances that are capable of splitting off or uniting with  $\text{H}^+$  ions. The acid and base concept may then be graphically represented thus:  $\text{S (acid)} \rightleftharpoons \text{B (base)} + \text{H}^+$  in which nothing is indicated concerning the other properties of S and B. When S and B are used in this way they may be spoken of as the *corresponding* acid and base.  $\text{AcOH (acid)} \rightleftharpoons \text{CH}_3\text{CO}_2^- \text{ (base)} + \text{H}^+$ ;  $\text{NH}_4^+ \text{ (acid)} \rightleftharpoons \text{NH}_3 \text{ (base)} + \text{H}^+$  and  $\text{COO}^- \cdot \text{CO}_2\text{H} \rightleftharpoons \text{COO}^- \cdot \text{COO}^- + \text{H}^+$  are discussed as examples of this equil. In general after discussing this conception and its applications at length B. concludes that the chem. character of acids and bases is most simply and comprehensively defined by the scheme:  $\text{acid} \rightleftharpoons \text{base} + \text{H}^+$ . The  $\text{OH}^-$  ion does not in general occupy any exceptional position as the bearer of the basic property. There is no logical basis for comparing the strength of acids with that of bases. The common conception of neutrality does not exist or in any case only on the basis of an arbitrary definition. The solvent, such as  $\text{H}_2\text{O}$ , therefore cannot be considered neutral. The acid-base and reduction-oxidation reagent equil. are analogous:  $\text{acid} \rightleftharpoons \text{base} + \ominus$  and  $\text{reducing agent} \rightleftharpoons \text{oxidizing agent} + \ominus$ . In the 1st case the positive and in the latter the negative electron are involved. E. J. WITZEMANN

**The anodic behavior of metals in non-aqueous solution. I. Nickel in methanol solution.** U. ŠKORGI. *Atti ist. Veneto* **80**, 1033-55 (1921).—Ni is electrochemically active in MeOH soln. of NaCl, a ppt. being formed at the cathode, presumably Ni methylate. The activity is almost complete in a KI-MeOH soln., I being formed at the anode, and the same product as above at the cathode.  $\text{CuSO}_4$  in MeOH gives almost complete activity at temps. above 15°, but at 0° it diminishes considerably. With  $\text{AgNO}_3$  soln. there is almost total passivity, although the oxidation of MeOH tends to reduce the polarizing effect of O. A. W. CONTIERI

**The anodic behavior of metals in non-aqueous solutions. II. Behavior of various metals in acetone solutions.** UMBERTO ŠKORGI AND PAOLO MARCHETTI. *Nuovo cimento* **22**, 151-75 (1921).—The study of a Ni anode in MeOH (cf. preceding abstr.) is extended to various metallic anodes in  $\text{Me}_2\text{CO}$  solns. of LiCl and  $\text{AgNO}_3$ . The expl. procedures were identical with those used previously by S. (*loc. cit.*), and the investigation included as anodes in  $\text{Me}_2\text{CO}$  solns. of LiCl and  $\text{AgNO}_3$ : (1) Ni, Co, Fe, Zn, Cu, Cd and Al in satd. LiCl soln. and (2) Ni, Co, Fe, Cu, Pb and Al in satd.  $\text{AgNO}_3$  soln. **LiCl solns.**—All metals were found to be bivalent except Cu and Al which were uni- and trivalent, resp. Various phenomena accompanied the attack of the metals, such as the formation of ppts., coloration of the solns., etc. With Ni, a ppt. was formed which was sol. in  $\text{H}_2\text{O}$  but could not be identified and was judged to be a  $\text{NiCl}_2 \cdot \text{LiCl}$  complex. No ppt. was formed with Co, Cd, Zn or Fe. With Cu, a white crust covered the anode, and was judged to be a  $\text{CuCl} \cdot \text{LiCl}$  complex, and a gas was evolved. This gas was due to the reaction  $(\text{CH}_3)_2\text{CO} + \text{Cl}_2 \longrightarrow \text{CH}_3\text{COCH}_2\text{Cl} + \text{HCl}$ , with electrolysis of the

HCl. With Al, a ppt. and a gas were formed, due perhaps to the  $(\text{CH}_3)_2\text{CO}$  dissociating:  $(\text{CH}_3)_2\text{CO} \rightarrow \text{CH}_3\text{COCH}_2^- + \text{H}^+$  and the Al then forming an  $\text{Al-Me}_2\text{CO}$  complex (the white ppt. at the anode). At the Pt cathode, together with the evolution of gas, deposition of Li and Li-acetone and the formation of ppts. contg. the metallic anode took place, due possibly to the reaction:  $(\text{CH}_3)_2\text{CO} + \text{Li} \rightarrow \text{CH}_3\text{COLi}:\text{CH} + \text{H}$ . *AgNO}\_3* solns.—No ppt. was formed with any metal, but evolution of gas occurred with Cu, Ni, Co, Fe, Pb and Al, all of which were passive under varying conditions. At the cathode, deposition of Ag took place. Cu was bivalent. In all cases including Cu, the passivity of the  $(\text{CH}_3)_2\text{CO}$  was in direct contrast to the behavior of aq.  $\text{AgNO}_3$  solns. of equivalent concns.

C. C. DAVIS

**Anodic behavior of metals in non-aqueous solutions. III. Iron, nickel, cobalt and chromium in alcoholic solutions of nitrates.** U. SBORGI AND G. CAPPON. *Nuovo cimento* 23, 303-31 (1922); cf. preceding abstrs.—S. and C. have used Co, Ni, Fe, and Cr metal dissolved in EtOH soln. of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NH}_4\text{NO}_3$ . Co is active in dissolving as a bivalent ion under all c. ds. from 0.03 to 3 amps./dm.<sup>2</sup> and temp. from  $-10^\circ$  to  $60^\circ$ . Ni is passive at all temps. up to  $25^\circ$ . At  $60^\circ$  there is partial ionization under high c. ds., i. e., 0.3 to 3 amps./dm.<sup>2</sup>. Under low c. ds. the Ni dissolves chemically in the warm EtOH soln. of  $\text{NH}_4\text{NO}_3$ . Fe is passive under all the above conditions. Cr is passive under low current pressures, but at high pressures  $\text{Cr}^{++}$  ions are formed. In all of these expts. a poorly conducting layer contg. some  $(\text{C}_2\text{H}_5\text{O})_2\text{Ca}$  is formed. In the cases where either partial or total passivity is noted, there is formed  $\text{O}_2$  representing about 7 1/2% of the total current; the rest, minus the current necessary to dissolve the metal, goes to form  $\text{C}_2\text{H}_5\text{CHO}$ .

A. W. CONTIERI

**Theory of electrolytic ions. XXVII. Simple method of determining the limiting molecular conductivity of strong electrolytes.** RICHARD LORENZ AND A. LANDÉ. *Z. anorg. allgem. Chem.* 125, 59-66 (1922); cf. C. A. 16, 1355.—The authors assume that strong electrolytes are completely ionized, and that the increase in cond. on diln. is due to an increase in the mobility of the ions. Thus, instead of the expression  $\mu = \alpha(u_0 + v_0)$ , the expressions  $\mu = (u + v)$  and for the limiting value  $\mu_0 = (u_0 + v_0)$  are obtained. The rate of increase of the mobility with diln., i. e.,  $u/u_0 = x$  and  $v/v_0 = y$ , is characteristic for each ion. The authors have, however, found that, for example,  $(1-x_R)/(1-y_{Cl}) = \text{const.} = a$ , similarly  $(1-x_{Na})/(1-y_{Cl}) = \text{const.} = b$ , and  $(1-x_{Na})/(1-y_K) = \text{const.} = c$ . These values are given as  $a = 1.079$ ,  $b = 1.396$ , and  $c = 1.292$ . These values are easily detd. for such salts as KCl and NaCl, which are therefore defined as normal electrolytes; hence, to find the limiting cond. of an acid, the Na or K salt is prepd., and in the case of a base, the chloride. Thus in the case of the anion  $A^-$ , the cond. of the K is detd. in at least two concns., e. g., at  $C_{1M} = K^+ + v_1$  and at  $C_{2M} = K^+ + v_2$  ( $K^+$  = ionic mobility of the K ion). If  $y = v/v_0$ , then from the above  $(1-x_1)/(1-y_1) = (1-x_2)/(1-y_2) = \text{const.}$ ; hence  $v_0$ , i. e., the limiting cond. of the anion, can be detd.

J. C. S.

**The theory of electrolytic ions. XXVIII. The theory of the determination of the limiting value of the molecular conductivity of strong electrolytes.** RICHARD LORENZ AND A. LANDÉ. *Z. anorg. allgem. Chem.* 126, 278-80 (1923).—The authors' empirical equations,  $(1-x_1)/(1-y_{Cl}) = \text{const.} = a$ ;  $(1-x_{Na})/(1-y_{Cl}) = \text{const.} = b$ ;  $(1-x_{Na})/(1-y_K) = \text{const.} = c = b/a$  (Lorenz and Landé, cf. preceding abstr.) can be derived from Hertz's theory (C. A. 6, 955) and holds for binary electrolytes in general. Here  $x$  and  $y$  denote, resp., for the cation and ion, the ratio of the mobility to the mobility at infinite diln. For a binary electrolyte  $(1-x)/(1-y) = S^+/S^- = \text{const.}$  for all concns., the value of  $S^+$  and  $S^-$  being dependent only on the nature of the ions. J. A. ALMQUIST

**Equilibria and reaction velocities.** W. F. BRANDSMA. *Chem. Weekblad* 19, 318-22 (1922).—The treatment of reaction velocities based on mol. collisions of substances in the gaseous state or in dil. soln. becomes difficult when the course of a reaction is not expressed by a simple equation, and exptl. results do not agree with theory. The conditions leading to equil. may be regarded from two points of view, the first dealing with the forces involved, that is, the energy units, and the second with space factors, that is, with entropy units. The factors deduced from the first vary inversely with the abs. temps., and so det. the temp. coeffs.; the entropy factors are independent of temp. This division is of great importance in org. reactions, since the theoretical treatment can take due account of both energy and space factors.

J. C. S.

**The velocity of a unimolecular reaction.** A. MCKEOWN. *Phil. Mag.* 46, 321-7 (1923).—Applying Einstein's conception of the mutual action of radiation and matter, and making use of a postulate advanced by Christiansen, an expression is obtained for the velocity const. of a unimol. reaction, which agrees formally with the empirical equation of Dushman (C. A. 15, 1443).

S. C. L.

**Note on the velocity of a unimolecular chemical reaction.** W. C. M. LEWIS. *Phil. Mag.* 46, 327-9(1923).—Assuming that the vol. of a unimol. reaction is a sym. oscillation and hence will absorb the energy passing through an area  $\lambda^2/\pi$ , where  $\lambda$  is the wave length of the radiation involved, Lewis develops an equation identical with Dushman's except for a numerical factor to which he attaches but little reliability. S. C. L.

**The velocity of absorption of carbon dioxide by ammoniacal solutions.** PAUL RIOT. *Compt. rend.* 176, 581-3(1923); cf. C. A. 17, 915. Curves show the velocity of absorption of  $\text{CO}_2$  in varying concns. of  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ , and  $\text{NaHCO}_3$  at  $20^\circ$  and the influence of temp. on the velocity of absorption of  $\text{CO}_2$  in varying concns. of  $\text{NH}_4\text{Cl}$  and of  $\text{NaCl}$ . The former decrease linearly; the latter pass through maxima. E. P. W.

**The velocity of action of halogens, oxygen and nitrogen upon metals as judged on the basis of their tempering colors.** G. TAMMANN. *Rec. trav. chim.* 42, 547-51 (1923); cf. C. A. 16, 2664. When an adherent layer of reaction product is formed upon a metal by the action of one of these agents the metal appears colored. These tempering colors change in the order of the Newton colors of thin air films. Since the thickness of the reaction layers cannot be measured these colors cannot be brought into quantitative relation with the air films. It was found that the isothermal thickening of the layer of the reaction product takes place in accordance with 2 quite different laws: the parabolic and the exponential law (cf. C. A. 15, 2617; 17, 14, 2985). The layers formed by the action of  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  on Ag, Cu and Pb thicken according to the parabolic law, and of  $\text{O}_2$  acting on Fe, Ni and Cu and of  $\text{N}_2$  on Ce and La according to the exponential law. On the basis of the formulas developed T. calcs. (1) the time in years in which the 1st visible yellow layer would be formed on the dry metal in air; (2) the initial velocities with which the oxide layers thicken,  $dy/dt = 1/ab$  in  $\mu\text{m}$  per min.; (3) the time in secs. after which an oxide layer corresponding to its equiv. air layer of  $14 \times 10^{-7}$  mm. would be formed. These data are given for Pb, Zn, Cd, Cu, Sn, Fe and Ni in a table. Oxide layers 1 mol. thick are formed very rapidly at  $15^\circ$  in dry air, within a sec. in most cases upon these metals, but this oxide layer protects the metal enormously. For this reason the apparent tempering (appearance of the 1st yellow) is exceedingly slow (required many years). If these 1st layers were not protective, metals would be extremely perishable and oxide layers would be scaling off continually. E. J. WITZEMANN.

**Velocity of formation of chloride from chloroform and alkali.** E. ABEL. *Z. Elektrochem.* 29, 391-4(1923). The velocity of formation of chloride from chloroform and alkali in homogeneous  $\text{EtOH}$  soln. is proportional to the  $\text{CHCl}_3$  content, but not to the alkali content. The velocity increases much more rapidly than the alkali concn. In very dil. alkali solns. the reaction is apparently of the 1st order, but the order increases with the alkali concn. H. JERMAIN CREIGHTON.

**"Transition temperature in chemical reactions."** CH. M. V. DEVENTER. *Z. physik. Chem.* 106, 155-6(1923).—A correction (cf. *Z. physik. Chem.* 1, 165; *Ber.* 19, 2142). H. JERMAIN CREIGHTON.

**Catalytic combination of ethylene and hydrogen in the presence of metallic copper.** II. Measurements of reaction velocity at  $150^\circ$ ,  $200^\circ$  and  $250^\circ$ . R. N. PEASE. *J. Am. Chem. Soc.* 45, 2235-42(1923); cf. C. A. 17, 2220.—The reaction is more nearly bimol. in the temp. region  $150$ - $250^\circ$  than at  $0^\circ$ , at which temp. it is approx. monomol. with respect to H and partially inhibited by excess of  $\text{C}_2\text{H}_4$ . Non-adsorption of the gases by the catalyst probably accounts for the more nearly normal character of the reaction at the higher temps. The temp. coeff. is much smaller at the higher temp. and is decreasing. H. JERMAIN CREIGHTON.

**Catalytic dehydroxidation of formic acid.** II. ERICH MÜLLER AND JOHANNES KEIL. *Z. Elektrochem.* 29, 395-99(1923); cf. C. A. 16, 3570.—The catalytic decompn. of  $\text{HCO}_2\text{H}$  to  $\text{CO}_2$  and  $\text{H}_2$  by Os depends on the latter having a high degree of dispersion. This is manifested by acting on the acid with a compd. of Os, which by reduction yields the metal in a highly dispersed and active form. The catalytic decompn. of  $\text{HCO}_2\text{H}$  by Os compds. shows an appreciable incubation period. Compds. of Os are more active catalysts for the decompn. of  $\text{HCO}_2\text{H}$  than Os which has been prepd. by the reduction of the oxide. H. JERMAIN CREIGHTON.

**Furfural from corncoobs.** III. Effect of catalysis on furfural yield in the steam digestion process. F. B. LAForge and G. H. MAINS. *Ind. Eng. Chem.* 15, 1057-60 (1923); cf. C. A. 17, 3184.—In the production of furfural from corncoobs, the addn. of 0.75% on the wt. of the coobs of  $\text{H}_2\text{SO}_4$  raises the yield to 10.9% as compared to 8.9% with  $\text{H}_2\text{O}$  alone. With 1.1% of  $\text{HCl}$ , a yield of 11.8% was obtained.  $\text{AcOH}$  gives a slight increase in yield, while  $\text{HCO}_2\text{H}$  considerably increases it. The addn. of 0.75%  $\text{H}_2\text{SO}_4$  and 2.4%  $\text{SO}_2$  gives a total yield of 12.3%. In all cases the yield increases up

to the optimum acid concn., and then drops off. The presence of Fe during the digestion lowers the yield in the same manner as when  $H_2O$  alone is used. T. S. CARSWELL.

**Application of recent ideas on atomic structure to the theory of surface catalysis.** HEBER GREEN. *Chem. Eng. Mining Rev.* 15, 410-4(1923).—A summary of the work from Davy (1817) to Langmuir and Baly (1921) on surface catalysis, with special emphasis on Langmuir's recent studies of the role played by monomol. films of gases condensed on solid surfaces. W. C. EBAUGH

**Promoter action in the decomposition of potassium chlorate.** H. A. NEVILLE. *J. Am. Chem. Soc.* 45, 2330-3(1923).—The fact that com.  $MnO_2$  is a more effective catalyst than c. p. material in the decompn. of  $KClO_3$  is ascribed to the presence of 8.8% of  $Fe_2O_3$  in the former. Expts. with mixts. of these two oxides confirm this view and show that each oxide is a promoter for the other. The action of  $CuO$  and  $MnO_2$  as mutual promoters is also demonstrated. JAMES M. BELL

**Catalytic oxidation of carbon monoxide. I. Efficiency of the catalysts, manganese dioxide, cupric oxide and mixtures of these oxides.** J. A. ALMQUIST and W. C. BRAY. *J. Am. Chem. Soc.* 45, 2305-22(1923).—Temp. efficiency curves have been obtained for 3 series of partially hydrated porous catalysts of  $MnO_2$  and  $CuO$ . Pronounced improvement in activity is caused by the addn. of small amts. of either oxide to the other. Partial dehydration is necessary to bring a catalyst to the region of max. activity, but the water content may then be lowered to a relatively small value by slow dehydration with but little change in the efficiency. Continued dehydration however finally lowers the efficiency, and causes loss of O (except in the case of  $CuO$ ). The efficiency of a catalyst is independent of the CO concn. between 0.1 and 0.6%, and is practically unchanged by the presence at high concn. of  $CO_2$ , the product of the reaction.  $H_2O$  vapor has a marked poisoning effect which is reversible. It is probable that under steady state conditions the O content of a catalyst is practically const., whether the catalyst is operating at low or high efficiency. A catalyst is reduced when treated with CO in the absence of O at a temp. at which it would act as a catalyst. The activity of a mixed catalyst is permanently impaired by this reduction even when much of the lost O is restored on subsequent operation as a catalyst. A theory for the mixt. effect is suggested in terms of the valence theory. The porous granules are believed to consist of a network of chains of atoms held together by valence forces. The forces that come into play at or in the film are also valence forces. When the catalyst contains the two oxides they will tend to neutralize each other's valence forces since they differ in basicity or polarity, and the strength of the valence forces at the film may be expected to be less than for a one-component catalyst. In other words, an increase in the rate of desorption or increase in the rate of a reaction within the film is attributed to what may be considered a partial chem. reaction between the two oxides. JAMES M. BELL

**Phase potentials.** EMIL BAUR. *Z. physik. Chem.* 106, 157(1923).—Polemical against Beutner (cf. C. A. 17, 2806). H. JERMAIN CRRIGHTON

**Equilibrium in the system of the four components, sulfuric acid, ammonium sulfate, lithium sulfate and water at 30°.** G. C. A. VAN DORP. *Rec. trav. chim.* 42, 765-74(1923).—The equil. at 30° in the 4 systems of 3 components that can be obtained from the 4 above-named compds. have already been described (Schfeinemakers, Cocheret, *Z. physik. Chem.* 59, 645; Van Dorp, *C. A.* 4, 2229; 8, 602). The diagrams and tabulated data for the 4-component system  $H_2SO_4-(NH_4)_2SO_4-Li_2SO_4-H_2O$  are given in this paper but cannot be satisfactorily abstracted. E. J. WITZEMANN

**The ternary system sulfur-selenium-tellurium.** L. LOSANA. *Gazz. chim. ital.* 53, 396-410(1923).—The single binary systems formed of S, Se and Te have been the subject of many accurate studies. The 3 binary systems were again examd. on the basis of previous results and data were obtained on some questions not previously clarified. Data and discussion on the thermal analysis of the ternary S-Se-Te system are given as well as results on the thermal and dilatometric study of mixts. of S with small amts. of Se and Te at the same time. The ternary system S-Se-Te shows no formation of compds. and there is no ternary eutectic. There are 2 zones of complete miscibility in which mixed crystals of Se and Te in S and of S and Te in Se are formed. The formation of mixed crystals of S and Te is greatly favored by Se, which provokes solid soln. with quite high percentages of Te. Many of these solid solns., however, show the phenomenon of more or less rapid "unmixing." The examn. of the variation of the 1st point of transformation of S showed that this is notably lowered by Se or Te and that this property of the 2 elements when both are present simultaneously is greater than the sum of the 2 lowerings when they are used separately. E. J. WITZEMANN

**Equilibria in systems with three components: water-acetic acid-tannic acid.** E. PATERNO. *Rec. trav. chim.* 42, 572-3(1923).—In previous work (*Gazz. chim. ital.* 43,

II, 245; cf. C. A. 8, 280) on this system a strange fact was noted. This system of 3 components in the same proportions has different properties depending on whether the  $H_2O$  is added to the binary system tannic acid-AcOH or whether AcOH is added to the tannic acid- $H_2O$  system. These 2 mixts. contg. the 3 components in the same proportions have different m. ps. P. has also crystd. AcOH from a concd. soln. of tannic acid in  $H_2O$ , which indicates that the tannic acid absorbs the  $H_2O$  so that it cannot hydrate the AcOH that is subsequently added. P. states that he will be unable to finish this investigation.

E. J. WITZEMANN

**Comparison of the dilatation curve and the thermic curve.** L. LOSANA. *Gazz. chim. ital.* 53, 393-50 (1923).—L. desired to det. whether the dilatometer previously described (Montemartini and L., C. A. 17, 2381) is capable of registering the singular points that occur in the usual cooling and heating curves in the thermal analysis of metallic alloys. With the methods and the app. usually used for the study of the thermal dilatation only substances in the solid state can be used. With the process here described fused substances may be used and the variations of vol. corresponding to the change of state may be followed. The method was tested with pure metals, with alloys having a eutectic, with a system that shows the formation of mixed crystals and with allotropic transformations. The results for the first 3 cases were satisfactory and are given in the form of curves. The study of allotropic transformations of S and  $NH_4NO_3$  was not so satisfactory on account of the difficulty of obtaining a bath with a temp. of about  $400^\circ$ .

E. J. WITZEMANN

**Thermal conductivities of some metals in the solid and liquid states.** W. B. BROWN. *Phys. Rev.* 22, 171-9 (1923).—A guard ring method of measurement was used. The conductivities of Sn and Cd decrease at the m. p. by over  $1/4$  and  $1/2$ , resp. For Ti there is a drop of about  $1/10$  at about  $120^\circ$ . The temp. coeffs. are about the same before and after melting, being  $-5 \times 10^{-5}$  (Sn),  $21 \times 10^{-5}$  (Cd),  $8 \times 10^{-5}$  (Ti). For the eutectics Sn 0.92 Zn 0.08, Sn 0.62 Pb 0.38, Pb 0.87 Sb 0.13, and Pb 0.46 Bi 0.54 the temp. coeffs. for the liquids are all positive consts. and have values at  $300^\circ$ , from 0.0011 (Pb-Bi) to 0.0030 (Pb-Sb), close to those found for gases at that temp., indicating that the mechanism is similar in the two cases. Below the m. p. the curves vary, one increasing with temp. (Sn-Zn), two decreasing and one reaching a max. (Pb-Sb). The sudden decrease on melting varies from  $2/3$  for (Sn-Zn) and (Pb-Sn) to  $1/10$  for (Bi-Pb). The results indicate a polymorphic change in Ti at  $120^\circ$ .

A. E. STEARN

**Experiments on the elevation of the critical solution temperature by additions.** CARL DRUCKER. *Rec. trav. chim.* 42, 552-50 (1923).—Earlier investigations by Schreinemakers and Timmermans do not show definitely whether or not the crit. soln. temp. of binary mixts. is influenced by small additions in accordance with colligative laws. The systems  $PhNH_2$ -hexane and  $CS_2$ -MeOH were investigated by detg. the critical soln. temps. first by the method of Rothmund (*Z. physik. Chem.* 26, 433 (1898)). This consisted in sealing known mixts. in 10-cc. tubes and detg. the temps. of the appearance and disappearance of the "clearing" when they were gently agitated in a thermostat. The same detns. were repeated with addition of  $H_2O$ , urethan, benzil, benzamide and thiocarbamide to the  $PhNH_2$ -hexane system and  $H_2O$ , KCl,  $HgCl_2$ , KBr, NaI,  $BaCl_2$ ,  $Ph_2NH$ ,  $CO(NH_2)_2$  and succinic acid to the other system. The effect was calcd. in terms of the quotient  $E$  obtained by dividing the observed temp. elevation due to the addition, by the no. of millimols. of the added substance per 1000 g. of solvent.  $E$  showed no constancy for the various compds. used such as is found in b. p. and m. p. elevations. In fact each compd. acts specifically. Some suggestions toward an interpretation are given (cf. also *Z. physik. Chem.* 68, 660 (1909)).

E. J. WITZEMANN

**The calorific value of carbon compounds.** DIMITRI KONOVALOV. *J. Chem. Soc.* 123, 2184-2202 (1923).—For many C compds. the heat of combustion, cor. for the heat of condensation of the resulting water vapor, is  $48.8n + X$ , where  $n$  is the number of atoms of O needed to be supplied for the combustion, and  $X$  is a characteristic number, the "thermal characteristic" for the substance. The significance of this formula lies in the behavior of  $X$ . It is zero for most members of the satd. series  $C_nH_{2n+2}$ , for liquid cyclic hydrocarbons  $C_nH_{2n}$ , for alic.  $C_nH_{2n+2}O$ , for liquid amines  $C_nH_{2n+3}NH_2$ , and for amorphous C itself, with an agreement to a few tenths  $\%$ .  $X$  is const. for most homologous series differing by  $CH_2$ , which means that for  $CH_2$  itself  $X = 0$ , and that the addition of  $CH_2$  does not alter the  $X$  of the rest of the mol. For the first member of a series, however, where there is no linkage between carbon atoms,  $X$  differs from the later values. These differences are multiples of 3. In some of these cases a substitution of  $CH_3$  for H lowers  $X$  by 9 units. With one possible exception, all values of  $X$  are multiples of 3, so that  $X$  can be written:  $3S$ . The const. 48.8 represents the calorific



value of amorphous C; the 3, the heat of transformation cryst.-amorphous; it is near the heat of crystn. of C. The values of  $X$  are given for numerous compds., as well as some rules for N linkages, etc.

W. P. WHITE

**The free energy and heat of formation of lead monoxide.** D. F. SMITH AND H. K. WOODS. *J. Am. Chem. Soc.* **45**, 2632-7(1923).—The free energy was detd. by means of a cell:  $H_2(g)/\text{dil. } Ba(OH)_2 \text{ soln.}/PbO(s) + Pb(s)$ , and the free energy of water. An app. is described for stirring, by electromagnetic aid, one limb of the cell in the absence of air, thus insuring full satn. of the liquid (with  $PbO$ ). The free energy at  $25^\circ$  is found to be  $-45,050$  cal., which differs by  $4000$  cal. from a value calcd. by Lewis and Randall from previous data. The heat of formation at  $25^\circ$  is derived as  $-52,560$  cal.

W. P. WHITE

**Cryoscopic measurements with nitrobenzene.** H. M. ROBERTS AND C. R. BURY. *J. Chem. Soc.* **123**, 2037-43(1923).—Nitrobenzene may be used as a solvent in f.-p. detns. only when unusual precautions are taken to prevent access of moisture or when the moisture content of the solvent is accurately controlled. The latter condition is reached when the solvent is in contact with salt pairs such as  $Na_2SO_4$  anhyd. and  $Na_2SO_4 \cdot 10H_2O$ , the di- and hexahydrate of  $SrCl_2$ , or  $H_2C_2O_4$  and  $H_2C_2O_4 \cdot 2H_2O$ . And conversely the vapor pressure of any salt pair can be detd. from the f. p. of nitrobenzene in contact with it. The f. p. of dry nitrobenzene is  $5.668 \pm 0.010^\circ$ . Nitrobenzene with its moisture content controlled by the salt pair  $Na_2SO_4 \cdot 0-10H_2O$  is an excellent cryoscopic solvent with  $K = 68.9$ , the av. of results where the solutes are naphthalene, *o*-chloronitrobenzene and  $\alpha$ -nitronaphthalene. This value is in close agreement with the value,  $68.7$ , calcd. from the latent heat of fusion.

JAMES M. BELL

**Normal cathode fall with graphite in gas mixtures.** A. GÜNTHER-SCHULZE. *Z. Elektrochem.* **29**, 370-3(1923).—The cathode fall with a graphite cathode in air is increased by volatilization of the electrode from  $339$  to  $361$  v., while in Hg vapor no change occurs. In mixts. of Hg-A the cathode fall follows exactly the simple arithmetical rule of mixts.; in H-A and O-CO mixts. the value lies below that calcd. by the rule of mixts.; in mixts. of Hg-O, Hg-CO, Hg-H, Hg-N, O-A, O-H and O-N the value lies above the calcd. value. The following mean values have been obtained for the cathode fall with graphite in different gases: Hg,  $452$  v.; O,  $371$  v.; CO,  $394$  v.; A,  $158$  v.; H,  $223$  v.

H. JERMAIN CREIGHTON

**Electro-endosmosis and the electrolytic transfer of water.** HEINRICH REMY. *Z. Elektrochem.* **29**, 364-70(1923); cf. C. A. **9**, 1869.—Since the ions are hydrated in aq. soln., it follows that on conducting an elec. current through a soln. of an electrolyte a transfer of  $H_2O$  must take place in the direction of the anode or the cathode, according as the anion or the cation is more strongly hydrated. The previous investigation is continued for the purpose of detg. the influence on electro-endosmosis of electrolytes at high concns. The amt. of  $H_2O$  transported increases as the concn. of the electrolyte decreases, and in cond.  $H_2O$  it amounts to  $23,000$ ,  $372$ ,  $373,000$ ,  $2350$  and  $886$  cc. per faraday, resp., with clay, animal charcoal, Zsigmondy's membrane, gelatin and parchment membranes. Thus parchment is an ideal membrane to use for differentiating between endosmotic and electrolytic transfer of  $H_2O$ , because at higher concns. of electrolyte the former is negligible in comparison with the latter. It is shown that in  $1.0$  and  $0.1$  *N* solns. the  $H_2O$  transferred is practically wholly due to a movement of the hydrated ions (with a parchment membrane). The electrolytic transfer of  $H_2O$  in  $1.0$  and  $0.1$  *N* solns. of a large no. of metal halides (and HCl) has been measured and the relative hydrations of the ions have been calcd.

H. JERMAIN CREIGHTON

**Electrical conductivity and the constitution of alloys. II. The system bismuth-thallium.** W. GUERTLER AND A. SCHULZE. *Z. physik. Chem.* **106**, 1-17(1923); cf. C. A. **17**, 2531.—The previous investigation has been extended to the system Bi-Tl. The results of cond. measurements confirm the complicated condition diagram of Bi-Tl alloys.

H. JERMAIN CREIGHTON

**The crystallization of certain salts in the magnetic field.** G. ROASSIO. *Private publication*, 20 pp., 1922; *Rev. géol.* **4**, 297(1923).—Using a Weiss electromagnet and the method of Meyer, R. has studied the crystn. of salts of Fe, Ni, and Co. He found that the magnetic field exercises an influence on (1) the orientation of the crystals, the angles between axes and lines of force varying with the substance, but being const. for a given compd.; and (2) the growth of the crystals, which become elongated in a definite direction, the angles remaining constant but again varying with the substance.

E. T. WHERRY

**The atomic moment of oxygen.** P. WEISS. *J. phys. radium* **4**, 153-7(1923); cf. C. A. **13**, 5.—Calcs. based on the ratio of the probabilities of electrons producing

a moment in the sense of the magnetic field acting perpendicular to the plane of the electronic orbits to those which give a moment in the opposite sense, give  $\sigma_0 = \sqrt{3}RC$ .  $C$  is the Curie const.  $= \sigma T/H$ ,  $R$  is the gas const.,  $\sigma$  is the magnetization of the gram-mol. and  $\sigma_0$  is the amt. of magnetization at satn. By substituting  $C = 0.03158$  (cf. Bauer and Piccard, *C. A.* 17, 2773) and dividing by the gram magneton, 1123.5, the no. of magnetons in O is 14.135 and the no. per atom is 9.992. The variation from whole nos. is within the limits of exptl. error.

H. M. McLAUGHLIN

**Simple method of measuring color.** A. R. O. MENSELL, *J. Am. Ceram. Soc.* 6, 777-82(1923).—Color is measured in three dimensions, hue, value, chroma. A general discussion only.

C. H. KERR

**The polarization of the light scattered by gases and vapors.** C. V. RAMAN AND K. S. RAO, *Phil. Mag.* 46, 426-34(1923).

S. C. L.

**Action of molybdic acid and molybdates on the rotatory power of malic acid.** E. DARMOIS, *J. phys. radium* 4, 49-70(1923); cf. *C. A.* 16, 2088; 17, 2561. A new interpretation of the work of Gerné is given. (Cf. *Compt. rend.* 104 112; *Bull. soc. physique* 1887 to 1891.) To a known quantity of each of a series of mixts.,  $(\text{MoO}_3)_n \cdot \text{C}_4\text{H}_4\text{O}_6$  (dextro), where  $n$  is 1, 1.5, 2, 2.5, 3, 4, 5,  $y$  parts of NaOH or  $\text{NH}_3$  were added and after diln. to 50 cc., the rotation  $[\alpha]$  was measured by means of a polarimeter through 2 dm. for the 3 rays of Hg. As shown by the curves representing  $[\alpha] = f(y)$  for each value of  $n$ ,  $[\alpha]$  increased with the addn. of NaOH or  $\text{NH}_3$  to a max. and then decreased rapidly. The curve for  $n = 2$  gave by far the highest max., which corresponded to  $2\text{MoO}_3 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{NaOH}$  and  $2\text{MoO}_3 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{NH}_3$ . The  $\text{NH}_3$  salt forms colorless, monoclinic crystals; parameters  $a:b:c = 1.442:1:1.939$ ;  $d_{100} = 97.16^\circ$ ; colored green, violet or sometimes orange by exposure to light.  $[\alpha]_{\text{D}}^{20}$  was 206° when  $C = 1$  and was almost const. at  $219^\circ$  when  $C > 7$ .  $[\alpha]_{\text{D}}^{20}[\alpha]_{\text{D}}^{20} = 2.26$ ;  $[\alpha]_{\text{D}}^{20}[\alpha]_{\text{D}}^{20} = 1.165$ . The hydrated crystals could be heated to  $120^\circ$  without decompn. The  $\text{NH}_3$  salt was very sensitive to the action of acids or bases. The Na salt was very sol. in water and the crystals were too small to be measured.  $[\alpha]_{\text{D}}^{20}$  was  $181^\circ$  when  $C = 0.95$  and  $208^\circ$  when  $C = 29.4$ . Decompn. did not occur up to  $100^\circ$ . The Ba salt has been prepd. Similar methods were used to establish the levorotatory compd.,  $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{NaOH}$ .

H. M. McLAUGHLIN

**The change in reaction on conversion of secondary and primary alkali phosphates into pyro- or metaphosphate. The alkalinity of borax solutions.** HANS MERSEHAUSER, *Biochem. Z.* 138, 6-12(1923); cf. *C. A.* 16, 2118. After conversion of  $\text{Na}_2\text{HPO}_4$  into  $\text{Na}_2\text{P}_2\text{O}_7$ , the mutarotation const. increased due to the increased alkyl. Conversion of  $\text{NaH}_2\text{PO}_4$  into metaphosphate had the opposite effect, which was further increased by conversion into  $\text{NaPO}_3$ ; these effects are due to the diminished acidity. In  $\text{Na}_2\text{P}_2\text{O}_7$  soln. the Lobry de Bruyn effect occurs. In borax soln., the final sp. rotation was less than  $52.8^\circ$  in proportion to the strength of the soln. (e. g., in  $1\% \text{ M}$  soln.  $[\alpha]_{\text{D}} = 42.5^\circ$ ; in  $1/100 \text{ M}$ ,  $[\alpha]_{\text{D}} = 51.5^\circ$ ), showing a sp. effect of borax on rotation by glucose.

GEORGE ERIC SIMMONS

**The dependence of the Hefner lamp on atmospheric pressure.** EMIL LIENERTHAL, *Z. Instrumentenk.* 43, 209-24(1923).—A survey of former work by L. (Z. *Instrumentenk.* 15, 157(1895)), Paterson (*J. Inst. Elec. Eng.* 38, 271(1906)), Batterfield, Haldane and Trotter (*Internat. Photometric Commission*, Zürich, July, 1911), Rosa and Crittenden (1914), Ott (1915) and Boltzmann and Basch (*Wiener Ber. Math. naturw. Kl. Abt. IIa*, 131, No. 1 (1922)) on the value of the coeff. of atm. pressure of the Hefner lamp with new detns. indicates that this coeff. is approx. 0.00015.

C. C. DAVIS

**The use of the helium light for refractometer measurements.** N. SCHÖRL, *Ber.* 56B, 1047-8(1923).—Answers (*C. A.* 10, 2663) gives directions for calcg. readings with the yellow He light into  $n$  for Na light. The directions are incorrect in 2 respects. In the first place the corrections are not negative as Answers states but are positive. Besides, the calcns. give not  $n_D$ , but the refractive index for the yellow He line. To calc.  $n_D$  from the readings with He light it is necessary to know the dispersion of the substance investigated not only for the yellow He line but also for the red and the green lines. Formulas are given to be used in making the necessary corrections.

HARRY B. WEISER

**Quantum theory.** R. F. HUNTER, *Chem. News* 127, 145-7, 166-9(1923).—This is a brief elementary review of the quantum theory, intended for chemists unfamiliar with the subject.

F. L. BROWNE

Crystals which have become isotropic (MÜGGE) 8.

## 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The electrical structure of matter. E. RUTHERFORD. *Nature* 112, Supplement No. 2811, 409-19; *Science* 58, 209-21; *Chemistry & Industry* 42, 874-82(1923).—An address.

Quantum theory of the normal photoelectric effect. W. BOHR. *Z. Physik* 17, 137-51(1923).—A mathematical discussion of the photoelec. effect and its bearing on the quantum theory.

Röntgen rays. E. FERMI. *Nuovo cimento* 24, 133(1922).—A summary of the work done on X-rays from the time of their discovery up to and including their use in the analysis of crystal structure.

Sources and marketing of radium. K. L. KITHIL. *Eng. Mining J.-Press* 116, 457-9(1923).

The crossed orbit model of helium. LUDWIK SILBERSTEIN. *Astrophys. J.* 57, 257-63; *Nature* 112, 53(1923).—A more detailed account of a foregoing paper (C. A. 17, 2668). Assigning further rational values of  $-\cos i$ , S. obtains the following correlation (in which the bracketed nos. cover no observed lines):

$$\begin{array}{ccccccccccc} \frac{5}{6} & \frac{4}{5} & \frac{3}{4} & \frac{2}{3} & \frac{1}{2} & \frac{1}{3} & \frac{1}{4} & \frac{1}{5} & \frac{1}{6} & \frac{1}{7} & \frac{1}{8} \\ 0S-1S & \gamma_1 & \lambda_2 & \lambda_3 & \lambda_4 & \lambda_5 & \lambda_6 & \lambda_7 & \lambda_8 & \lambda_9 & \lambda_{\infty} \end{array}$$

$\lambda_{\infty}$  (=512.3) has not been observed but may be confidently expected. For  $-\cos i = \frac{1}{2}$  ( $\lambda = 601.2$  calcd.) Lyman has found the single peculiar line exptly. at  $\lambda = 600.5 \pm 0.3$ . The "combination line" 0S-1S should be at  $\lambda = 601.3$ . In every other case alternate values of  $-\cos i$  correspond to the Lyman series 0S-mP. G. L. CLARK

A static model of the hydrogen molecule. H. STANLEY ALLEN. *Proc. Roy. Soc. Edinburgh* 43, II, 180-96(1923).—A theory of the constitution of mols. is developed on the basis of the "quantum force" introduced by Langmuir with a view to securing a static model of the H atom. The "quantum force" is assumed to vary inversely as the cube of the distance and to be a repulsion or an attraction according to the sign of the elec. charges between which the force acts. On this assumption a H mol. is possible, having many of the properties of the mol. imagined by Bohr but with the electrons at rest relatively to the H nuclei. Various configurations of equil. are theoretically possible, but not all of these are stable. The most stable configuration appears to be that in which the nuclei and electrons are situated at the corners of a square whose diagonal is 0.871 Å. long, and whose moment of inertia is  $6.261 \times 10^{-41}$  g. cm.<sup>2</sup> The work that must be done completely to disintegrate the mol. corresponds to a p. d. of 30.06 v. Another configuration gives values agreeing exactly with those obtained from Bohr's model of the H mol. In the case of the charged H mol. with only one electron the distance between the nuclei is 1.239 Å., and the ionization potential is 17.34 v. A possible configuration is suggested for a triat. H mol. in which the nuclei and electrons are situated at alternate corners of a regular hexagon.

A contribution to the dynamo-kinetic theory of the atom and the electron. TIT TOMMASINA. *Compt. rend.* 176, 892-4(1923).—A speculative paper, proposing as the ultimate unit of the electron and of all matter an entity called the "energon." This is supposed to be a minute portion of matter, whose nature is left undefined, but whose sole important property is its energy which is indestructible and which gives to the electron and positive nucleus all their properties.

The life history of an  $\alpha$ -particle. ERNEST RUTHERFORD. *Nature* 112, No. 2808, Supplement 305-12; *Engineering* 117, 769-70(1923).—A lecture before the Roy. Soc. summarizing the recent work done by R. and his pupils on the ionization along the path of the  $\alpha$ -particle.

The stopping of  $\alpha$ -rays in liquids and vapors. K. PHILIPP. *Z. Physik* 17, 23-41(1923).—Normal liquids show a stopping power for  $\alpha$ -particles in accordance with Bragg's law of additivity. Associated liquids exhibit a value abnormally high. The stopping power of solns. depends on the relative concns. of the components.

The theory of the motion of  $\alpha$ -particles through matter. I. Ranges. II. Ionization. R. H. FOWLER. *Proc. Cambridge Phil. Soc.* 21, 521-30, 531-40(1923).—I. This consists of a crit. survey of the theory of ionization of atoms by  $\alpha$ -particles of Henderson, who had based his conclusions on a strict interpretation of the quantum theory. F. shows that if the modern values of the ionization and resonance potentials be intro-

duced into Henderson's theory the stopping powers of the gases for  $\alpha$ -particles are markedly less than they should be. That is, the  $\alpha$ -particles on this theory lose energy two-thirds as rapidly as they are observed to in air. For He the discrepancy is still greater. F. then concludes that one must go back to the ideas of the original theory of Bohr based on classical dynamics (cf. C. A. 7, 936; 9, 1269), in which energy is lost by the  $\alpha$ -particles to electrons in the orbits of atoms without the electron being displaced from its orbit. For the old Bohr theory accounts for the observed stopping power quantitatively. If one does not one must assume that the energy of the particle must be lost much more freely than is to be expected from classical theory. H. F. then turns to the Bohr theory of ionization produced along the path of the  $\alpha$ -particle. Bohr had assumed that a good portion of the ionization along the path of the  $\alpha$  particle was due to the ionization produced by the faster electrons knocked out of atoms by the  $\alpha$ -particles. He estd. the ionization produced in this way by assuming that all the fast electrons which were given an energy  $(S + 1)\lambda$  by the  $\alpha$ -particles produced  $S$  pairs of ions, where  $\lambda$  is the ionizing potential. This led Bohr to values of the ionization produced which were somewhat greater than those experimentally observed. F. points out that this is not correct as the fast electron may give more than 7 in energy to any electron it ionizes. He uses statistical methods to get a rough notion of the order of magnitude of the correction to be introduced for such a behavior. Putting in the rough numerical value obtained, he shows that the ionization observed in air and He lies within the theoretical limits of error of the corrected Bohr values. He points out that in all these cases the theoretical values in He differ from the observed by too great an error to be explained by the minor discrepancies in the theory. Thus the stopping power and ionization computed for He is one-half as great as that observed. He suggests that an explanation of this is to be found in the results of Millikan, who observed that near the end of the range the  $\alpha$ -particle produces one doubly ionized He atom for every six singly charged pairs of ions formed. F. shows that by correcting for the singles produced by the secondary electrons, nearly three-fourths of the He atoms ionized by  $\alpha$ -particles in Millikan's expts. are doubly ionized. If it be assumed that every ionization by an  $\alpha$ -particle produces a doubly charged ion, then the stopping power and the ionization computed for He on Bohr's theory agree with expt. L. B. LOEB

**Adsorption of the --B and --C members of the radium and thorium series by ferric hydroxide.** J. A. CRANSTON AND R. HUTTON. *J. Chem. Soc.* 123, 1318 24(1923); cf. C. A. 17, 923.--Under similar conditions the ratio of Th B/Th C adsorbed by Fe(OH)<sub>3</sub> is greater than the ratio of their isotopes Ra B/Ra C, even when the initially different relative concns. of the solns. are taken into account. The interval of time between prep. the solns. and the carrying out of the adsorptions has been found to be an important factor in detg. the ratio adsorbed. The influence of this time factor is in quant. agreement with the theory advanced to explain the greater proportion of the --C member adsorbed with lapse of time. In 0.001 N acid soln. a small proportion of the --B and --C members exists as negative colloid and is in a state suitable for adsorption by the positively charged Fe(OH)<sub>3</sub> hydrosol. The colloidal B members form aggregates of negative charge, and with lapse of time decay gradually into the --C members, which are held in these colloidal aggregates, and are adsorbed owing to the predominating influence of the remainder of the --B members. Thus, as time goes on, the proportion of --C atoms in a suitable state for adsorption is increased in a regular manner. JAMES M. BELL

**Long-range particles from radium active deposit.** G. KIRSCH AND H. PETTERSSON. *Nature* 112, 394-6(1923).--A new method has been developed for obtaining strong and const. source of  $\alpha$  radiation. Dry Ra emanation mixed with O<sub>2</sub> is enclosed in thin-walled capillaries of hard glass, lined with Al-foil 12 $\mu$  in thickness. Silica may be used as long range particles are given off by the glass. Sc, V, Co, As, and In, the first 3 as oxides, the last 2 as metallic mirror and as chloride, resp., do not give long range particles (>30 cm. air) to a greater no. than  $3 \text{ or } 4 \times N \times 10^{-4}$ , where  $N = \text{no. of } \alpha\text{-particles from Ra C discharged per sec. within the capillary.}$  By use of a different emanation vessel so arranged that the substance to be examd. is spread on Cu foil of about 4 cm. absorbing power fairly conclusive evidence is obtained that H-particles are given off by Si, as element, range <18 cm., Be as oxide, <12 cm., Mg as oxide, <13 cm., Li as carbonate, <10 cm. air. W. ALBERT NOYES, JR.

**The size of the electron as determined by the absorption and scattering of X-rays.** F. K. RICHMYER. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 87-8(1922).--Data on the mass absorption coeff. of Al previously reported by R. and more recently by Duane indicate a much smaller size for the electron than that calcd. from A. H. Compton's formula based on a ring electron. S. K. ALLISON

**Electron emission from thoriated tungsten filaments.** I. LANGMUIR. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 107-8(1922).—In filaments of W contg. Th at high temps. the Th by diffusion forms an adsorbed surface layer on the W, covering a fraction  $\Theta$  of the surface. The log of the electron emission is a linear function of  $\Theta$ , as expected from theory. An equation is given for the change in  $\Theta$  due to heat treatment. Results show that surface Th atoms evap. from underlying Th atoms much more readily than from underlying W atoms.

S. K. ALLISON

**Secondary electron emission from nickel.** C. DAVISSON AND C. H. KUNSMAN. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 110(1922); cf. *C. A.* 16, 379.—Using the method of Millikan and Barber, D. and K. have measured the total no. of secondary electrons emitted from Ni per primary bombarding electron.

S. K. ALLISON

**Researches on the collision of electrons.** R. RUDY. *Rev. gén. sci.* 34, 470-5(1923).—I. A review of the work of Townsend (cf. *C. A.* 17, 1751) on ionization by collision. II. A brief review of the researches of Franck and Hertz (cf. *C. A.* 8, 614, 3526) on electronic collisions and the work of Lenard (*Ann. Physik* 8, 149(1902)) on the measurement of electronic velocities.

L. M. HENDERSON

**The question of the electrical charge of submicroscopic particles.** THEODOR SEHL. *Z. Physik* 16, 34-41(1923).—A crit. discussion of some of the attempts made to ascribe the results of Ehrenhaft on the detn. of the subelectron, to the unknown density, shape, and surface layers of the submicroscopic particles used by Ehrenhaft. S. concludes that neither the expts. of Schiller purporting to explain the subelectrons of Ehrenhaft as due to deviations of the particles from spherical form, nor of Bär to explain them by densities less than those assumed for the particles used, nor the theory of Kaufmann-Regener ascribing them to adsorbed gas layers on the particles, are capable of withstanding a crit. examn. He further concludes that the only solution lies in an expl. study of the laws of fall of such submicroscopic particles in which the expts. are completely devoid of any connection with the constitution of electricity.

L. B. LOEB

**Theory of the positive column in discharge tubes.** A. PARTZSCH. *Z. Physik* 14, 191-203(1923).—A new law is deduced between the variation of the potential gradient in the positive column with pressure. This is done by assuming that the no. of new ions generated by collision for a tube of given diameter, and for a current of given intensity, are independent of the pressure, and then applying Townsend's theory for ionization by collision to it. The new law deduced agrees with expt. more closely than those deduced from previous theories. From the measurements on this effect, and P.'s theory values are obtained for the product  $NV$  of Townsend ( $N$  the no. of impacts per cm., and  $V$  the mean ionizing potential), which are little different for those given by Townsend from measurements on the ionization by photoelectrons. Deviations observed in the measurements in  $N_2$  are ascribed to the presence of  $H_2$  in the gas used. The no. of ionizing impacts per cm. are of the same order of magnitude for  $H_2$  and  $N_2$ . From the values of this quantity the value of the efficiency of the positive column as a source of light was estd. The values obtained differ but little from those observed by Ångström. On a principle of similarity proposed by Holm P. was able to include the effect of the change in diameter of the tube in his equation for the change of the gradient with pressure. The values from this equation agree satisfactorily with the observed values for the effect of change of tube diameter.

L. B. LOEB

**Photoelectric conductivity and chemical combination.** B. GUDDEN AND R. POHL. *Z. Physik* 16, 42-5(1923).—An extension of Fajan's work on the photoelec. cond. of various compds. Among those studied are the fluoride, nitrate, sulfate, carbonate, chloride, bromide, iodide, oxide, sulfide and selenide of Pb, Ti, Hg, Cd, Ag, Zn, Cu, Ba, Sr, Cu, Mg, K and Na. No photoelec. conducting fluoride, nitrate or sulfate was found and but 2 carbonates,  $PbCO_3$  and  $Ti_2CO_3$ . Of the alk. earths only the sulfides show the phenomenon.

HARRY B. WEISER

**Ionization and activation of gases.** K. T. COMPTON. *Trans. Am. Electrochem. Soc.* 44 (preprint).—Gases may be ionized in several ways, as by the photoelec. effect of short wave length radiation, by impact of high-speed electrons, by high temp., and by certain chem. reactions. Accompanying phenomena are discussed which may give the gas new properties and which must be considered to insure an adequate explanation of conduction and radiation in gases. The most striking spectroscopic and elec. properties are produced by: mol. compds. of monat. gases, the effect of ionization in changing chem. and spectroscopic properties to the type characteristic of the next group in the periodic table, band spectra of metallic vapors and monat. gases, absorption of subordinate series lines, fluorescence and resonance radiation. The catalytic action of a gas whose atoms are in an excited state upon another gas with which it is mixed

may be photochem. or not depending on whether light or another agent is used to put atoms into the excited state.

W. H. BOYNTON

**Ionization in moist and dry air.** J. J. NOLAN AND J. T. HARRIS. *Proc. Roy. Irish Acad.* 36, 31-49 (1922); cf. *C. A.* 15, 2780.—The composite nature of the ionization in moist air has been demonstrated by the "air-current method" and by the "alternating-field method." The effect of extreme drying has been investigated. The effect on negative ionization is to increase the numbers of ions of the more mobile type, and cause the disappearance of the ordinary ions. With positive ionization, the more mobile ions are also found in greater numbers, although the ordinary ions are still present. Doubly charged positive ions are found in very dry air. Some indications are obtained of the presence of free electrons.

E. H.

**Critical velocities of electrons in krypton and the excitation of the spectra of this gas.** GEORGES DEJARDIN. *Compt. rend.* 176, 894-7 (1923). Using a 3-electrode tube of a type described in previous investigations in A plus He D. dets. the crit. velocities of electrons in pure Kr. He obtains for the ionization potential  $12.7 \pm 0.2$  v., and for the double ionization potential  $28.25 \pm 0.5$  v. on the basis of single ionization for  $A = 15.2$ . Apparent ionization was observed at pressures of about 1 mm. at 9.8 v. This was assumed to be ionization by "successive impacts," that is, ionization due to the impact of low velocity electrons on atoms in resonating or excited state. He then studies the appearance of the 2 spectra of Kr, the red and the blue, as a function of the potentials to which the electrons had been accelerated. The former spectrum appears between 12.7 and 9.8 v., depending on the pressure and current density. Above 28.25 v. at low pressures (0.001 mm.), certain lines of the blue spectrum appear. From 30 to 34 v. other of the lines of the blue spectrum appear, and the color of the discharge becomes markedly blue at 30 v. At 0.1 mm. intense lines of the secondary spectrum appear at about 15.5 v. This is practically the difference in potential between the double and single ionization potentials. This potential then corresponds to the loss of a second electron by atoms ionized at 12.7 v.

L. B. LOEB

**A note on the electromagnetic mass of the electron.** E. C. STOKER. *Proc. Cambridge Phil. Soc.* 21, 552-5 (1923).—A simple mathematical treatment of an apparent conflict between the value of the mass of an electron deduced from ordinary electrodynamics, and that deduced from the theory of relativity. If  $W_e$  is the electrostatic energy of the electron, ordinary methods give for the mass,  $m_0 = \frac{1}{4} W_e / c^2$ , where  $c$  is the velocity of light. Relativity theory gives  $m_0 = W_e / c^2$ , where  $W_e$  is the total energy of the electron. This suggests that the electron possesses energy other than the external electrostatic energy of amt.  $\frac{1}{4} W_e$ . It is shown that if the electron is held in equl. by a system of tensions producing a force  $2\pi\sigma^2$  per unit area, it would possess internal potential energy of precisely this amt.

L. B. LOEB

**Theory of electron emission.** SAUL DUSHMAN. *Trans. Am. Electrochem. Soc.* 44, (preprint); cf. *C. A.* 17, 3282.—The Nernst heat theorem is applied to the evapn. of electrons. The theoretical treatment, analogous to that for the evapn. of a monat. substance, leads to an equation for the electron emission from metals as a function of the temp. Exptl. data show the emission from various metals to agree with the new equation.  $I_V = 60.2 T_s^2 - (b_0 - 4.39 \sqrt{kV})/T$ . With cathode field strengths sufficiently intense to cause  $b_0$  to decrease to approx. 0,  $I_V = 60.2 T^2$  and the electron emission no longer follows an exponential law. Several curves and tables are shown.

W. H. BOYNTON

**Heisenberg theory of the anomalous Zeeman effect.** G. BREIT. *Nature* 112, 396 (1923); cf. *C. A.* 16, 3632.—H. assumes that the atom is made of 2 parts, (a) the shell and (b) the valence electron. If the magnetic field of the electron induces a precession in the shell, then the field due to the shell induces a precession in the electron. There will be no contribution to the energy of the elec. field since the radius of the orbit is unchanged. On this hypothesis the  $2p_1$  state has the lower energy, while the reverse is actually the case. If there were no induced precession in the shell, but if the electronic precession should be hypothesized, the  $2p_1$  and  $2p_2$  levels would coincide. If there is no induced precession the  $2p_1$  level is the state of higher energy in agreement with expt. This is doubtful because it presupposes that the dimensions of the orbits in the  $2p_1$  and  $2p_2$  states are the same. Similar difficulties for the triplet terms are encountered.

W. ALBERT NOYES, JR.

**The effect of a magnetic field on the absorption of X-rays.** J. A. BECKER. *Proc. Am. Phys. Soc.* 1922, *Phys. Rev.* 20, 115 (1922).—The absorption coeffs. of Al, C, Cu, Fe, Ni, Pt, Zn, Ag are very little affected by a magnetic field of 18,000 gauss when X-rays of short wave length are used. This is in agreement with the idea that the

magnetic properties of atoms are detd. by the outer electrons, which are not affected by short X-rays. S. K. ALLISON

**Magnetic and natural rotatory dispersion in absorbing media.** E. O. HULBURT. *Phys. Rev.* **22**, 180-7(1923).—An extension of H.'s theory (*C. A.* **15**, 3587; **16**, 1362) to take into account absorption. By making certain approximations, simplified formulas are obtained which give the rotation for wave lengths sufficiently removed from the crit. wave length, provided the  $n$  and the extinction coeff. conform to the Lorentz dispersion equations with one resonance frequency. The equation of magnetic rotation in isotropic media agrees closely with exptl. results for  $\text{CS}_2$  and  $\alpha$ -monobromonaphthalene. It is suggested that the theoretical equation for natural rotation  $\theta/l = r_1 + (2\pi^2\gamma_1/\lambda^2) \cdot [\mu_0^2 - 1/(1 + k_0^2)]$  (where  $\mu_0$  and  $k_0$  are  $n$  and extinction coeff. resp., and  $r_1$  and  $\gamma_1$  are consts.) may be assumed to describe the phenomenon in any medium, whether  $\mu_0$  and  $k_0$  satisfy the Lorentz dispersion equations or not, but this has not yet been tested experimentally. A. E. STEARN

**Remarks concerning the mechanism of magnetic phenomena.** J. DORFMANN. *Z. Physik* **17**, 98-111(1923).—A discussion of magnetic susceptibilities from the standpoint of at. structure. Metals have larger magnetic susceptibilities than their corresponding ions owing to the presence of the valence electrons. The selective absorption of long waves by ferromagnetic substances is considered from the standpoint of electronic rather than nuclear rearrangements. The interpretation of the Curie point from the standpoint of the absorption of heat energy by the atoms is discussed.

**The action of an electron tube under the influence of a magnetic field.** W. BRAUNBEK. *Z. Physik* **17**, 117-36(1923).—A theoretical discussion of the effect of a magnetic field on the motion of electrons in a tube so constructed that the anode is a cylinder with a single wire cathode in its axis. The magnetic field is parallel to the axis. The field has the effect (1) of decreasing the no. of electrons emitted from the filament through increasing the space charge; (2) of decreasing the electron current through sending some of the electrons back to the cathode; (3) of changing the ratio of grid to plate current. With a positive grid potential the sharp increase in electron emission due to the higher grid potential becomes negligible in its effect upon the plate current. Measurements verifying these points were made. W. ALBERT NOYES, JR.

**The scattering of X-rays at small angles.** A. R. DUANE AND WM. DUANE. *Proc. Am. Phys. Soc.* **1922**, *Phys. Rev.* **20**, 86-7(1922).—The amt. of X-radiation scattered by reflecting substances at angles less than the min. angle at which reflection can occur is very small. By making corrections for the natural leak of the ionization chamber and for stray radiation, it is found that the radiation scattered from a sheet of Al at angles less than that at which the min. wave length of the incident beam is reflected, is less than 1% of the intensity at the max. of the general radiation curve. Thus scattering from Al may be treated largely as reflections from planes. From the crit. angle at which radiation begins to be reflected, and the min. wave length in the incident beam which may be calcd. from the voltage used, the value of  $d$  for Al is found to be 2.32 Å., in close agreement with Hull's value of 2.33 Å. S. K. ALLISON

**An experimental verification of the theory of Röntgen-ray spectra resulting from multiple atomic ionization.** A. DAUVILLIER. *Compt. rend.* **177**, 167-9(1923); cf. *C. A.* **16**, 1537.—D. advances a hypothesis to account for the complexity of high frequency spectra of the light elements. He states that the supplementary lines observed correspond to some combinations taking place between levels. The lower level of a combination shows a different energy value than usual. D. suggests that these supplementary lines would not appear if the intense ionization produced by the cathode rays could be avoided. These lines should not appear in the fluorescence spectrum. The K series of iron was investigated and it was shown that the doublet  $\text{K}\alpha_1\alpha_2$  was not excited under these conditions. The existence of hypothetical levels of ionization is indicated by the work of Mohler and Foote on high ionization potentials of the vapors of P, S, and Cl. True lines of ionization seem to become less marked in the L series. L. M. HENDERSON

**The diffraction of X-rays by "smectic" substances.** M. DE BROGLIE AND E. FRIEDEL. *Compt. rend.* **176**, 738-40(1923).—Friedel (*C. A.* **17**, 3633) has shown that between, the amorphous and cryst. states of matter there exist 2 intermediate stages characteristic of anisotropic liquids: (1) "nematic," in which the mols. are distributed at random, but all have a common direction ("cholesteric" is a sub-group in which torsion is apparent); and (2) "smectic," in which the mols. have a common direction and are arranged in equidistant parallel layers. If true, (1) will not diffract X-rays, while (2) should reflect them in a manner similar to that by a set of parallel planes in a crystal.

In order to test this conclusion a mixt. of K oleate, glycerol and  $H_2O$  (found by Perrin and Wells to be "smectic" with a distance between mol. layers of 42.4 Å.) was tried with the  $K_{\alpha}$  radiation of Cu. The inter-layer distance was found to be 43.5 Å. Analogous results were obtained with  $NH_4$  oleate.

G. L. CLARK

**The X-ray investigation of fatty acids.** ALEX MILLER. *J. Chem. Soc.* 123, 2043-7(1923).—De Broglie and Friedel (preceding abstr.) pointed out that the long  $CH_2$  chains in the mols. of paraffin wax could be detected by means of X rays. An X-ray spectrometer was used, and photographs were taken of the reflection lines obtained with capric, lauric, myristic, palmitic, stearic, and behenic acids. The spacings existing in these substances, as shown by their reflection lines and measurements, increase in length as the no. of  $CH_2$  groups increases.

G. H. RHOADS

**Low-velocity X-ray electrons.** LEWIS SIMONS. *Phil. Mag.* 46, 473-80(1923). The normal component of more than 85% of the electrons emitted from an Au film under the influence of a heterogeneous beam of X-rays is less than 2 v. The distribution with velocity bears a relation to that of thermions from a hot body. The mode of production of these slow electrons can hardly be due to at. recoil consequent on the ejection of a rapid  $\beta$ -ray nor to the action of the transformed X-ray energy into longer wave lengths. The analogy with the thermionic process probably arises from the fact that in both cases only the outermost system of electrons takes part in the action, though the mechanism of the two processes must differ considerably, the intermediary being the rapid  $\beta$ -ray. The velocity distribution of electrons, from the thermionic point of view, corresponds in the case investigated to 11,000° abs. It is important to investigate this correspondence under all conditions. A "null" method of using an electro-scope is described.

S. C. LUND

**X-ray spectroscopy as a means of qualitative and quantitative chemical analysis.** D. COSTER. *Chem. News* 127, 65-70(1923).—The X-ray emission from the anticathode of an X-ray tube consists of two essentially different parts: (1) the heterogeneous radiation depending only on the voltage and (2) the characteristic radiation or line spectrum which characterizes the elements present on the anticathode. The range of wave lengths which can be measured in the present state of X-ray spectroscopy lies between 13.5 and 0.1 Å. X-ray spectroscopy has some advantage over optical spectroscopy: (1) The X-ray spectra are simpler; (2) it is of no importance in what mixts. or compounds the element in question occurs; (3) one  $\frac{1}{2}$ % of a certain element, of which only 1 mg. is available, is enough to be detected. It has been used successfully by C. and others in the examn. of Hf in Zr minerals and some details are given of the procedure and sources of error. A main feature of the method is the addn. to the substance to be examd. of a known quantity of an element with an at. no. in the neighborhood of that element and the detn. of the X-ray spectrum of the mixt. By comparison (Moll microphotometer) of the intensity of the lines of the added element to that of the corresponding lines of the element under investigation an estm. of the concn. of the latter element can be obtained.

A. L. SCHUBEN

**Direction of  $\beta$ -rays produced by polarized X-rays.** F. W. BURN. *Nature* 112, 363(1923).—B. reports on a set of photographs taken by him which support the following conclusions of Wilson (*Nature* 112, 26; cf. *C. A.* 17, 3450): (1) that partial polarization of the primary X-ray beam is indicated by the direction of ejection of the  $\beta$  rays produced by it being in the plane which includes the exciting beam and the path of the cathode rays in the X-ray tube; (2) that the majority of the long range tracks have a large forward component as compared with the lateral component.

S. K. ALLISON

**The excitation of spectral lines by the collision of electrons.** G. HEITZ. *Naturwissenschaften* 11, 778-9(1923).—Results of expts. are outlined, to be published elsewhere in detail, which confirm the views of Bohr in regard to the necessary conditions for the appearance of spectral lines.

C. C. DAVIS

**The origin of spectra (recent progress).** J. C. McLENNAN. *Chem. News* 127, 198-202, 212-3(1923).—An address.

E. J. C.

**The spectrum analysis of the rare earths.** J. M. EDER. *Ann. Physik* 71, 12-18 (1923).—E. has been engaged for many years in the study of the rare earths La, Pr, Nd, Sm, Eu, Gd, Tb, Y, Dy, Ho(Nh), Er, Tu, Cp and Ce. The spectra of Ce, La, Pr and Nd are well known but the others need further study. The characteristics of the spectra of these rare earths are briefly reviewed.

A. L. SCHUBEN

**Multiplets in the spectrum of vanadium.** OTTO LAPORTE. *Naturwissenschaften* 11, 779-82(1923).—Preliminary data are given in tabulated form on multiplets in the V spectrum.

C. C. DAVIS

**Series spectra in oxygen and sulfur.** J. J. HOPFIELD. *Nature* 112, 437-8(1923).—With the vacuum grating spectrograph new lines have been observed in the extreme



ultra-violet spectra of O and S. For O the new lines constitute the triplet series  $0P_{123} - mS$ ,  $0P_{123} - mD$ , and  $0P_{123} - 1s$ , of which 7, 6, and 1 members, resp., have been observed. For S the new lines are grouped into series similar to those occurring in O, the no. of members observed for each series being 3, 3, and 1. In both spectra the line  $0P_1 - 1s$  is definitely absent, probably representing a prohibited combination. The new results indicate that if the  $0P_{123}$  level is the valence level then the resonance and ionization potentials are 9.11 v. and 13.56 v. for O, and 6.50 v. and 10.31 v. for S.

C. C. KIESS

**Infra-red spectroscopy.** V. P. LUBOVICH AND MISS E. M. PEAREN. *Proc. Trans. Roy. Soc. Canada* [3] **16**, 195-212(1922).—By means of a thermopile and galvanometer the absorptions of alc. solns. of the 6 photosensitizing dyes dicyanin, dicyanin A, pinacyanol, nigrosine SS, alizarin blue S, and Eastman red sensitizer 700, were observed. Also the transmissions of 6 filters were measured, to det. what combination of dyes and filters would allow photography of the infra-red. The results indicate that photography should be possible with light rays of wave lengths up to 20,000 Å. Plates sensitized with dicyanin were used to photograph the red and infra-red spectra of Hg, Sn, Pb, Bi, Zn, Sb. The new data not only check previously observed wave lengths but in addn. yield new ones. A thalofide cell was employed to measure the intensities of some infra-red lines and also to verify their existence.

C. C. KIESS

**The regularities of the spectral lines of iron, and the atomic magnetic field.** H. NAGAOKA AND Y. SUGIURA. *Nature* **112**, 359(1923).—By observing regularities in the behavior of spectral lines of Fe in the Stark effect, N. and S. have succeeded in arranging a few lines between  $\lambda 2400$  and  $\lambda 3000$  Å. into regular triplets, quartets, and sextets. In addn. to this, some of the lines can be arranged in quadruplets in which the frequency difference between the first pair is the same as that between the last pair. With the assumption that the observed septs. are due to a Zeeman effect of the at. magnetic field, the field strength is calcd. to be  $6.6 \times 10^4$  gauss, in agreement with values found by Weiss from expts. on magnetization of Fe. It is suggested that the complexity of the spectra of the ferromagnetic metals may be due to the Zeeman effect of an intense at. magnetic field.

S. K. ALLISON

**The variation of the increased dielectric constant of illuminated zinc sulfide with temperature.** J. HERWIG. *Z. Physik* **16**, 23-8(1923).—To decide whether the binding of the electrons to the S atoms postulated by Lenard for the excited ZnS was a loose one, or whether the increase of the dielec. const. by illumination was ascribable merely to the increased mobility of the transient photoelec. liberated electrons in the sulfide, H. measured the change of the increased dielec. const. of excited ZnS with temp. The expts. showed that there was too much phosphorescent luminosity even at liquid air temps. to make the expts. decisive. Had drop in luminosity been comparable with the decrease of the abnormal dielec. const. induced by illumination at temps. below  $211^\circ$  abs., this decrease must have been interpreted as being due to the increased mobility of the transient electrons only, and not to a loose binding by the S atoms whose binding would be unaffected by temp. From  $211^\circ$  abs. on down the luminosity and the dielec. const. decreased very sharply. At  $371^\circ$  abs. the luminosity and the dielec. const. reached a max. value, falling again rapidly at  $533^\circ$  abs.

L. B. LOEB

**Radiation measurements on platinum and tungsten.** R. HENNING AND W. HEUSE. *Z. Physik* **16**, 63-70(1923).—The authors give a new method for measuring the emissive power of incandescent metals, and describe a micropyrometer with which they carried out measurements on Pt and W. The emissive power of the metals was found to be independent of the temp. (for Pt between room temp. and  $1710^\circ$ , and for W between  $2000^\circ$  and  $3200^\circ$ ). The values obtained are for 6470 Å. and 5360 Å., resp.: Pt 0.348, 0.363; W 0.49, 0.49. The m. p. of W was found to be  $3370^\circ$ .

L. B. LOEB

**The absorption spectra of the vapors of various quinones.** J. E. PURVIS. *J. Chem. Soc.* **123**, 1841-9(1923).—The absorption spectra of the vapors of *p*-benzoquinone, toluquinone, *p*-xyloquinone, thymoquinone, dichlorothymoquinone, dibromothymoquinone,  $\alpha$ -naphthaquinone, and anthraquinone were investigated, with a Welsbach incandescent light in the visible regions and a condensed Cd spark for the ultra-violet regions. Each substance was introduced into a 200-mm. tube with quartz ends, the tube filled with dry  $CO_2$ , and observations were made at various temps. and pressures, and varying time exposures. 68 bands were observed in the vapor of *p*-benzoquinone, lying between  $\lambda 490$  and  $\lambda 232$ , 10 groups of bands between  $\lambda 490$  and  $\lambda 380$  with toluquinone, 10 bands between  $\lambda 470$  and  $\lambda 370$  with *p*-xyloquinone, 8 bands between  $\lambda 470$  and  $\lambda 390$  with thymoquinone, and no narrow vapor bands with the other compds. investigated. Hence, the increasing complexity of the *p*-benzoquinone compds. means the gradual disappearance of the narrower vapor bands.

G. H. RHODES

**The carbon arc spectrum in the extreme ultra-violet.** II. F. SIMMON. *Proc. Roy. Soc. (London)* **104A**, 368-75 (1923).—The spectrograph used in the previous work (*C. A.* **17**, 1188) has been furnished with new gratings ruled with a very light pressure as recommended by Millikan. As a consequence the C arc spectrum has been photographed to wave length 371.5 Å., giving practically all the lines observed by Millikan in the spectrum of the hot spark, and about 25 more are lines than were previously reported. The shortest arc line is at 386.1 Å.; it appears when the exciting potential between the electrodes is at 40 v. but not at 30 v. It thus appears that the L series of C can be excited by a potential closely in accord with the 35 v. required by the quantum relation. C. C. KIESS

**The dispersion of light in the ultra-violet spectrum by gaseous substances.** JOHN KOCU. *Arkiv Math. Astron. Fysik* **18**, No. 3, 15 pp (1923). The interference method and app. used in previous work (*C. A.* **7**, 2711; **9**, 884) have been employed to measure the refractive indices of NO and N<sub>2</sub>O. The wave lengths for which index measurements were made were those emitted by a quartz Hg lamp between 5462 Å. and 2447 Å. The observed dispersions of both gases are very poorly represented by the simple Cauchy formula, and therefore sep. formulas involving 4 consts. are called for each to represent the new results within the errors of observation. C. C. KIESS

**Stages in the excitation of the spectra of thallium.** F. L. MOHLER AND ARTHUR E. REARK. *J. Optical Soc. Am.* **7**, 819-30 (1923).—Elec. measurements in Tl vapor at 600° reveal a first resonance potential of 0.9 v. and a first ionization potential of 6.04 v. Measurement of the photoelec. effect of the total radiation yielded a higher crit. potential of 12.4 v. Spectrograms of the excited vapor at the various stages show the development of the arc spectra. In the unexcited state of the atom the series electron occupies the  $2p_{1/2}$  orbit. The least energy it can absorb is 0.962 v. in the transition from  $2p_{1/2}$  to  $2p_{3/2}$ , which is a metastable state because the reverse transition  $2p_{3/2} \rightarrow 2p_{1/2}$  with emission of radiation is forbidden by the selection principle. Various potentials below ionization result in the emission of the 2 subordinate series  $2p_{1/2} \rightarrow m$  and  $2p_{3/2} \rightarrow m$ . The lines emitted after the crit. potential 12.4 v. is reached are among those usually attributed to the spark spectrum. The evidence indicates, however, that these lines belong to a 2nd arc spectrum produced by a 2nd type of single ionization, the removal of 1 of the 2  $6p_{1/2}$  electrons. C. C. KIESS

**Quanta of light, diffraction and interference.** LOUIS DE BROGLIE. *Compt. rend.* **177**, 548-50 (1923).—An attempt to explain the manner in which light quanta undergo diffraction and produce the phenomenon of interference. C. C. KIESS

**The scattering of light by dust-free liquids. Changes with temperature.** W. H. MARTIN AND S. LEHRMAN. *J. Phys. Chem.* **27**, 558-64 (1923). The effect of change in temp. on the light scattered was observed with benzene, heptane, and naphthalene. The intensity of the scattering increases with temp. and passes through a very great value at the crit. temp., falling off again rapidly above the crit. temp. The scattered light is more nearly plane polarized towards the crit. temp. but is never completely plane polarized. HARRY B. WEISER

**Refraction and absorption of light in zinc blende at temperatures up to 700°.** MARIA MELL. *Z. Physik* **16**, 244-65 (1923). The clear-colored greenish yellow and yellow Zn blende shows normal dispersion in the visible region of the spectrum. On increasing the temp. the  $n$  increases, the change being most marked with longer wave lengths. The permeability of the blende increases with increasing wave length. The min. in the red depends on the impurity mixed with the Zn blende. The permeability decreases with increasing temp. The absorption moves from the ultra-violet into the visible region and the bands in the red due to impurities are displaced toward the longer wave lengths. HARRY B. WEISER

**Absorption spectra of nitrosylsulfuric acid and of the complex compounds of copper sulfate and of ferrous sulfate with nitric oxide.** II. I. SCHLESINGER AND ALBERT SALATHE. *J. Am. Chem. Soc.* **45**, 1863-78 (1923).—The absorption spectra of nitrosyl-sulfuric acid dissolved in H<sub>2</sub>SO<sub>4</sub> of various concns. show that appreciable quantities of the former remain undecomposed when the H<sub>2</sub>SO<sub>4</sub> is diluted to 50% and that at higher concns. of H<sub>2</sub>SO<sub>4</sub> relatively large amts. of nitrosylsulfuric acid are present. This result is contrary to one of the fundamental assumptions made by Raschig (*C. A.* **5**, 2912) in developing his theory of the lead chamber process. Absorption spectra of the complexes formed by FeSO<sub>4</sub> with NO in solns. of H<sub>2</sub>SO<sub>4</sub> of various strengths support the view that there are two such complexes, both of the compn. FeSO<sub>4</sub>·NO, and show that one of them is stable when the H<sub>2</sub>SO<sub>4</sub> has a concn. above 65% and the other when the concn. of the acid is below 50%. Spectra of the complex CuSO<sub>4</sub>·NO are found to be identical with those of the so-called ferrous and cupric nitrosulfonates. The ab-

sorption spectrum of nitrosulfonic acid is very similar to that of  $\text{FeSO}_4 \cdot \text{NO}$  in concd.  $\text{H}_2\text{SO}_4$  soln., a result which supports the view that possibly nitrosulfonic acid should be looked upon as an unstable soln. of a complex compd. of  $\text{H}_2\text{SO}_4$  and  $\text{NO}$ . Examn. of the spectra of solns. of  $\text{HNO}_3$  in concd.  $\text{H}_2\text{SO}_4$ , before and after heating the solns., has shown that  $\text{HNO}_3$  is not readily decompd. in such solns. into nitrosylsulfuric acid, at least if the soln. is not very concd. with respect to  $\text{HNO}_3$ . The character of the absorption spectrum of nitrosylsulfuric acid favors the view that this substance is present in soln. largely as nitrosulfonic acid.

JAMES M. BELL.

The "break" spark spectra and their use in chemical analysis. C. AUER VON WELSBACH. *Ann. Physik* 71, 7-11(1923).—v. W. found that greater precision in spectrum analysis, especially with the rare earths, has been obtained with the vibrator type of induction coil in which the "make" spark introduces small particles of the pole substance into the space between the poles and the "break" spark vaporizes them with the result that the spectrum observed is quite free of air lines. The necessary spectroscopic app. has been described in detail in an earlier communication (*C. A.* 17, 1764). For convenience in identifying lines in the visible spectrum a transparency contg. the spectra of a large no. of elements is brought into coincidence by a suitable arrangement with the spectrum under observation in the spectroscope. This greatly simplifies the identification of spectrum lines of the substance under test.

A. L. SCHOEN.

Note on the illumination of the spectroscope with end-on vacuum tubes. T. R. MERTON and R. C. JOHNSON. *Phil. Mag.* 46, 448-9(1923).—In order to secure uniform illumination of the prism or grating from a tube in end-on position it is proposed to silver the outer walls of the capillary. Comparison shows the advantage both in intensity and uniformity of illumination.

S. C. L.

Phosphorescent and fluorescent substances. W. JENISCH. *Umschau* 25, 388-91(1923).—A survey of the methods of prepn. and properties of different classes of phosphores and fluorescent substances together with a discussion of the modern theories that are offered to account for the luminescence. The light energy falling on a phosphore splits off electrons from the activating metal. According to Lenard the S atom takes up these electrons and then gives them up slowly to the activating metal, the latter process being accompanied by luminescence that may persist for some hrs. The important role attributed to the S atom is shared also by Se and O atoms.

HARRY B. WEISER.

A simple method of preparing good phosphorescing zinc sulfide. JULIUS SCHMIDT. *Ber.* 55B, 3988-9(1922).—Equal parts by wt. of pure  $\text{ZnSO}_4$  and  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_2$  are dissolved in hot  $\text{H}_2\text{O}$  and pptd. hot by  $\text{H}_2\text{S}$ . The  $\text{ZnS}$  is allowed to settle, partly washed with hot  $\text{H}_2\text{O}$  by decantation and finally transferred to a suction filter where the washing is completed. After drying on a  $\text{H}_2\text{O}$  bath 200 g. of the sulfide is soaked with a soln. contg. 20 g.  $\text{MgCl}_2$  and 10 g. each of the chlorides of Ca, Sr and Ba in 200 cc.  $\text{H}_2\text{O}$  mixed with 10 cc. of an  $\text{NH}_4$  tungstate soln. contg. 0.004 g. of the salt per cc. The mixt. is evapd. to dryness on the  $\text{H}_2\text{O}$  bath, transferred to a Hessian crucible, heated gradually in a Roszler gas furnace to a red heat at which temp. it is held 30-40 min. After cooling, the sol. salts are washed out by decantation and the  $\text{ZnS}$  remaining is dried on a  $\text{H}_2\text{O}$  bath. It gives a strong green phosphorescence.

HARRY B. WEISER.

The influence of an electric field on the increase of the dielectric constant observed in illuminated zinc sulfide. J. HERWEG. *Z. Physik* 16, 29-33(1923).—H. investigates the influence of a superposed elec. field on the increased dielec. const. of an excited phosphorescent  $\text{ZnS}$ , and observes some curious phenomena. He finds that the dielec. const. of the sulfide which is initially increased by illumination is decreased slightly by a superposed field. With a direct field a peculiar polarization sets in which is not present with an alternating p. d. of 50 cycles. The decrease of the dielec. const. is directly proportional to the field, and it requires a certain min. value of the field to produce any lowering. With decaying phosphorescence the polarization does not occur. The polarization may find its explanation in a close parallel existing between the observations of F. Schmidt on the *flashing up* of the phosphorescence in an elec. field, and the present phenomenon.

L. B. LOEB.

The luminescence of flames. WALTHER GERLACK. *Naturwissenschaften* 11, 782-3(1923).—A short discussion of the work of Sentfleben (*C. A.* 10, 419) and Noyes and Wilson (cf. *C. A.* 17, 22).

C. C. DAVIS.

Luminescence of organo-magnesium halides. R. T. DUFFORD, S. CALVERT and DOROTHY NIGHTINGALE. *J. Am. Chem. Soc.* 45, 2058-72(1923).—Grignard reagents in  $\text{Et}_2\text{O}$  soln. are chemiluminescent on oxidation by  $\text{O}$  only if the Mg is attached directly to an unsatd. C atom. No chemiluminescence is found with Zn or Hg. The luminescence is influenced by several factors, which are given and some specific cases of very

bright luminescence are noted. Two tables are given listing the luminescent properties of more than 60 compds.

E. P. WIGHTMAN

**Some cases of the analogous action of radiations and of ozone on chemical and colloid reactions.** A. FERNAU. *Kolloid-Z.* **33**, 89 (1923). Röntgen, ultra-violet, and  $\alpha$ -radiations cause the coagulation of  $\text{Ce}(\text{OH})_3$  sols and of albumin sols and the inversion of cane sugar sols. These same results are produced by means of  $\text{O}_3$  or  $\text{H}_2\text{O}_2$ . These radiations also produce  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$ . Conclusion: The coagulation of the positively charged  $\text{Ce}(\text{OH})_3$  sol is brought about by electrons set free when  $\text{O}_3$  reverts to  $\text{O}_2$ , the coagulation of the albumin by its dehydration, and the inversion of the sugar by the energy of the excited  $\text{O}_2$  mols.

F. L. BROWNE

**The influence of ultra-violet radiation in the presence and absence of catalyzers on the reactivity of a halogen bound to the carbon ring.** K. W. ROSENMUND, K. LUXAT AND W. TIEDEMANN. *Ber.* **56B**, 1950 (1923).—The comparative inertness of a halogen in an aromatic compd. has been overcome in the presence of Cu or Cu compds. at 180–220°. At a temp. still lower so that the catalyzing action of the Cu is only very slight, the radiation from a quartz Hg vapor lamp has a decidedly accelerating effect on the reaction  $\text{C}_6\text{H}_5\text{COOH} + \text{KOH} = \text{HOC}_6\text{H}_4\text{COOH} + \text{KCl}$  in the absence of Cu, and is still more active in its presence. At a lower temp. still, 101°, the Cu is inactive both alone and under radiation, though the radiation itself is still an accelerating agent. This shows that the radiation acts directly upon the org. mol. rather than upon the Cu. Other reactions give similar results.

G. R. FONDA

**The photochemical reduction of zinc sulfide.** ANDREA JOH AND GUY ERNSCHWILLER. *Compt. rend.* **177**, 313 (1923).—All varieties of white  $\text{ZnS}$  which blacken under the influence of light must be heated; must contain at least traces of impurities either metals or metalloids; and must not be entirely anhyd. Chemists have usually attributed the slate color of the exposed sulfide to the presence of Zn. This view has been established experimentally by allowing the light from a Hg arc to act on  $\text{ZnS}$  suspended in  $\text{H}_2\text{O}$  in a quartz vessel, whereby several eq. of Zn as well as S were formed. H was also liberated in the process due in part to the action of the Zn on  $\text{H}_2\text{O}$  and in part to the formation of  $\text{H}_2\text{S}$  which was decomposed by light. Some Zn salt of a thionic acid was also formed in the process. The sulfides affected were all phosphorescent and the rapidity of the darkening was found to vary as the product of two factors: the intensity of the phosphorescence and the hygroscopicity. The sulfide with certain impurities is rendered metastable by calcining. Suitable radiations striking these metastable mols. change them to a crit. state and under ordinary conditions when the sulfide is anhyd. they go back to the metastable condition with the emission of light. However, if the sulfide is hygroscopic, hydrolysis results with the formation of  $\text{H}_2\text{S}$  and  $\text{Zn}(\text{OH})_2$ . During the exposure a crit. mol. of sulfide acts on the hydroxide likewise sensitized by light. Instead of returning to the metastable state the sulfide reduces the hydroxide, giving Zn and  $\text{H}_2\text{SO}_3$ . The latter reacts with  $\text{H}_2\text{S}$  giving  $\text{H}_2\text{O}$ , S and  $\text{H}_2\text{SO}_4$ .

HARRY B. WEISER

**Temperature coefficients of reactions in tropical sunlight.** NIL RATAN DHAR. *J. Chem. Soc.* **123**, 1856–61 (1923); cf. *C. A.* **12**, 111; **16**, 3793. Temp. coeffs. in direct tropical sunlight were detd. for the following reactions, and compared with the values in the dark, obtained in previous investigations: on  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ ;  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{MnSO}_4$  and  $\text{H}_2\text{SO}_4$ ;  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{KMnO}_4$ ,  $\text{MnSO}_4$ , and  $\text{H}_2\text{SO}_4$ ;  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{I}_2$ ;  $\text{NaHCO}_3$  and  $\text{HgCl}_2$ ;  $\text{NaHCO}_3$  and  $\text{I}_2$ . The temp. coeff. was in all cases decreased by an amt. increasing with the degree of acceleration by light. The action of light is therefore similar to that of a positive catalyst. The reaction of  $\text{K}_2\text{C}_2\text{O}_4$  with  $\text{I}_2$  is semi-mol. with respect to  $\text{I}_2$ ; the semi-mol. equation,  $k = 2(\sqrt{a} - \sqrt{a-x})/t$ , may be applied to other photochem. reactions. The results are considered in connection with the radiation hypothesis of chem. reaction.

BURT H. CARROLL

**Photochemical production of formaldehyde.** E. C. C. BALY, I. M. HEILBRON AND W. F. BARKER. *Nature* **112**, 323 (1923).—A letter in reply to Spechr (*C. A.* **17**, 2237).  $\text{CH}_2\text{O}$  can be detected (Schryver test) when cooled sols. of  $\text{CO}_2$  are exposed to ultra-violet radiation ( $\lambda = 220\mu$ ) for 18–72 hrs. It is essential that the distance between the lamp and the soln. be 6 in. or more or that a calcite screen be interposed. The amt. of  $\text{CH}_2\text{O}$  formed is 1–2 parts in 100,000 and is increased if the soln. contains Ca or  $\text{KHCO}_3$ .

ARTHUR LOCKE

**Influence of drying on photochemical reactions.** HEINRICH TRAMM. *Z. physik. Chem.* **105**, 356–401 (1923).—An app. is described for the purification and dehydration of a series of gases by fractional distn. at the temp. of liquid air. The degree of dehydration attained lies below 0.004 mm.  $\text{H}_2\text{O}$  vapor pressure. The influence of moisture on the photochem. formation of  $\text{O}_3$ ,  $\text{HCl}$ ,  $\text{SO}_2\text{Cl}_2$  and  $\text{COCl}_2$ , as well as on the photochem.

decompn. of HCl, HBr and HI, has been studied. Combination does not take place in a very dry mixt. of  $H_2$  and  $Cl_2$  which is free from  $O_2$ . In a  $CO-O_2$  mixt., which has been dried to such an extent that combination takes place in the dark but very slowly, even at high temps.,  $CO_2$  is formed in ultra-violet light with a velocity comparable with that in a moist explosive mixt. of the gases. Traces of both  $SO_2$  and  $H_2O$  retard the decompn. of  $CO_2$  in ultra-violet light. Contrary to the assumption that in the thermal  $CO-O_2$  reaction the accelerating effect of  $H_2O$  vapor is due to the intermediate formation of formic acid, it is shown that at flame-temp., in accordance with the Nernst heat theorem, only a very small quantity of formic acid is present, and that this cannot be accepted as the cause of the violent reaction which follows. This conclusion is supported by the fact that a formic acid- $O_2$  mixt. is non-explosive, while an equiv. mixt. of  $CO$ ,  $H_2O$  vapor and  $O_2$  is explosive. A mixt. of  $H_2$  and  $O_2$  of such purity and dryness has been prepd. that it does not explode in a glass vessel heated to redness, but combination only takes place slowly. While the thermal combination of these gases can be markedly retarded by drying, the velocity of union in ultra-violet light is independent of the degree of dryness.

H. JERMAIN CRIGHTON

**The action of canal rays on photographic plates.** EMILE MÜHLESTEIN. *Compt. rend. suisse de phys. Bâle* 1921; *Arch. sci. phys. nat.* 3, 294-5(1921); *Physik. Ber.* 4, 34.—Solarization phenomena produced on AgBr-gelatin plates by canal rays were attributed to layers about  $0.33\mu$  thick, rendered impenetrable by the canal rays. These layers could be recognized under the microscope by their structure. This view is substantiated by obtaining a reversal when the plate is first fixed and subsequently developed in daylight. The phenomenon of multiple reversal, which shows itself in a darkening on the inside of bright solarization regions, is caused by an agglomeration of dark star-shaped crystals. These are produced by the developer, which can penetrate the gelatin "skin" after it has become "cracked" by long exposure. A. E. STEARN

**Chemiluminescence.** RUDOLF WEGSCHEIDER. *Rec. trav. chim.* 42, 585-7(1923).—The evolution of light, as the result of a chem. reaction, which cannot be explained by the temp. is called chemiluminescence. In this case a chem. reaction is a permanent transformation of isolable products into others that can be isolated. W. considers 2 types of chemiluminescence: (1) A portion of the energy liberated in the reaction is converted into radiation at once. The point of origin of this radiation is the at. group which is formed by the union of the mols. required for the reaction and the rearrangement of which gives rise to the chem. reaction. Since the radiation is not given off by the reagents used or the reaction products but from an intermediate product the radiation may be different from that which the reagents or the products can emit and may not correspond to any isolable chem. individual. (2) A portion of the energy liberated in the reaction may be transferred to mols. which up to this time have not been involved in the reaction and causes them to emit light. In this case only such radiations as correspond to definite chem. individuals are emitted. Such a case was investigated by Haber and Zisch (*C. A.* 16, 2809); Lifschitz, Kallerer, (*C. A.* 17, 495) who passed Na vapor dild. with  $N_2$  into  $Cl_2$  gas which gave a flame showing the D-line of Na. W. reviews and discusses these expts. in some detail. E. J. WITZEMANN

**The photochemical transformation of fluorescing solutions of dyes.** PETER PRINGSHEIM. *Z. Physik* 16, 71-6(1923).—Eosin solns. that are highly sensitive and relatively insensitive possess identical capacities for light absorption and fluorescence. In the sensitive solns. fluorescence and chem. reaction are produced by light from the same region of the spectrum and both processes can be brought about by pure monochromatic light. The results are not in accord with those of Weigert.

HARRY B. WEISER

**The question of polarized light from dye solutions. II.** S. I. VAVILOV AND V. I. LEVSHIN. *Z. Physik* 16, 135-54(1923); cf. *C. A.* 16, 2637.—From a study of 26 dyes it was found that the fluorescence of aq. solns. of all dyes which give a clear fluorescence light is practically unpolarized. On the other hand weakly fluorescing dyes give out a strongly polarized light in accord with Weigert's observations. In glycerol soln. all the dyes investigated emit a strongly polarized fluorescent light. The degree of polarization is the same for all except Rhodamine B and G. In such viscous colloidal media as colloidion, celluloid in acetone, gelatin in  $H_2O$ , etc., the behavior is the same as in alc., acetone or water. The degree of polarization does not depend on the wave length of the fluorescent spectrum and it is greater with natural than with polarized light.

HARRY B. WEISER

**Contribution to the action of light on silver bromide.** RAGNAR STRÖMBERG. *Z. wiss. Phot.* 22, 165-76(1923).—With a microbalance having a sensitivity of  $27(10)^{-7}$  mg. per scale division, no diminution in the weight of a AgBr film under illumination

from a Nernst glower could be observed at pressures of 145 mm. or 0.001 mm. Hg. The apparent diminutions that took place were found by blank expts. to be due to thermal effects.

G. R. FONDA

**The temperature coefficient of photochemical reaction rate.** R. C. TOLMAN. *J. Am. Chem. Soc.* 45, 2285-96(1923).—A simple equation for the temp. coeff. of photochem. reaction rate has been derived on the basis of the quantum theory. It agrees with one previously obtained by using the methods of the classical statistical mechanics. This equation successfully interprets existing data and shows that Plotnikov's division of photochem. temp. coeffs. into 3 distinct classes is apparently untenable. An equation for change of temp. coeff. with frequency has been derived and successfully applied to existing data. The apparent deviations from Einstein's law of photochem. equivalence have also probably been accounted for.

W. P. WHITE

**The action of traces of impurities on the photochemical synthesis of phosgene.** J. CATHALA. *Bull. soc. chim.* 33, 576-81(1923).—It has been shown by Chapman and others that the presence of O retards the photochem. synthesis of  $\text{COCl}_2$ . To get rid of all O C. heated the reaction mixt. to  $850^\circ$  to  $1000^\circ$ , which is above the dissociation temp. of  $\text{COCl}_2$ . Under those conditions O combines with CO forming  $\text{CO}_2$ . A retarding action was observed even after the removal of O, which is attributed to the presence of a trace of  $\text{CO}_2$ . A quant. study is promised.

HARRY B. WEISER

**Influence of adsorbed substances on the spectral sensitiveness of silver bromide.** W. FRANKENBURGER. *Z. physik. Chem.* 105, 273-328(1923).—Full details of an investigation, the results of which have been published previously (*C. A.* 17, 1382).

H. JERMAIN CREIGHTON

**Electrostatic calculations based on the preceding paper.** K. F. HERZFELD. *Z. physik. Chem.* 105, 329-32(1923); cf. preceding abstr.—A mathematical paper, in which is calcd. the influence of the surroundings on the work required to transfer an electron from a negative Br ion to a positive Ag ion in the AgBr crystal.

H. J. C.

**The decomposition of nitrosyl chloride in light.** A. KISS. *Rec. trav. chim.* 42, 665-74(1923).—According to the radiation theory of reaction velocity reactions that proceed with considerable velocity at ordinary temps. are brought about by the infrared radiation due to the temp. of the reacting materials. According to this the reaction for the formation of NOCl should be a true dark reaction insensitive to visible light. The expts. here described showed that the velocity of NOCl formation remains unchanged when illuminated by white light. The decomn. of NOCl in white light is a monomol. reaction. The temp. coeff. of the velocity consts. between  $0^\circ$  and  $78^\circ$  is 1.

E. J. WITZERMANN

**Partial and consecutive reactions in the photosensitive system: quinine sulfate, chromic and sulfuric acids.** G. S. FORBES, J. C. WOODHOUSE AND R. S. DEAN. *J. Am. Chem. Soc.* 45, 1891-5(1923).—With 2 photochemically activated reactants the total reaction velocity should be the sum of 4 partial reactions with 4 different velocity consts. One involves 2 activated mol. species, another only unactivated species, and 2 others involve 1 activated and 1 unactivated species. It is shown how species known to be activated in some reactions may give no evidence of activation in others. The concn. of a photochemically unactivated reactant is shown to be without effect upon the velocity of a photochem. reaction provided that its concn. is not so small that its reaction with activated reactants does not become the slow stage of the total process.

JAMES M. BELL

**Hatchettolite and associated minerals from Hybla, Ont. (WALKER, PARSONS) 8.** Ellsworthite and associated minerals from Hybla, Ont. (WALKER, PARSONS) 8. Application of recent ideas on atomic structure to the theory of surface catalysis (GREEN) 2. Change of pleochroism of kunzite by Becquerel rays (PRZIBRAM) 8.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**High-frequency electric induction furnace.** R. DUFOUR. *Compt. rend.* 176, 828-30(1923).—The uses and advantages of high-frequency induction furnaces are briefly discussed.

C. C. VAN VOORHIS

**Electric furnace operation.** ANON. *Elec. World* 82, 727(1923).—Discussion of costs, linings, suitable size, etc. by a number of elec. furnace experts.

C. G. F.

**A cheap electric resistance furnace of the tube type.** HUBERT FORESTIER. *Bull. soc. chim.* 33, 999-1000(1923).—This device has the advantage of exposing the object

heated directly to the radiation of the wires and thus reducing the thermic inertia of the app. About a metal tube (3-4 cm. diam.) there is rolled a sheet of paper on which the resistor nichrome is wound. The wire is then covered with a thin layer of alundum (1-2 mm.), and this is dried. When dry, the tube is placed vertically in the axis of a cylinder made of asbestos board of 10-12 cm. diam. and quick-setting cement is poured into the space; the whole is then left in the open air for 2 hrs. Asbestos packing 3-4 cm. thick is applied; the paper is calcined by electricity and the metal tube withdrawn. This furnace can be heated to 1000° in 30 min. and cooled back to 100° in 1.5 hrs. It consumes 4.5 amp. at 110 volts, or about 1/2 kw. GEORGE C. O. HAAS

**The mechanism of the electric arc.** A. M. TYNDALL. *Phil. Mag.* **46**, 330-1 (1923).—Reply to Duffield (*C. A.* **17**, 2836). S. C. L.

**The electrothermic metallurgy of zinc.** B. M. O'HARRA. *Bur. Mines, Bull.* **208**, 106 pp. (1923); cf. *C. A.* **17**, 688.—The elec. furnace for smelting offers obvious advantages in the way of the efficient utilization of energy, large units, easy attainment of high temps. and the possibility of treating complex ores. The author describes and discusses at length the numerous elec. furnace Zn processes proposed and tried out, giving cost figures and many valuable operating data. It is concluded that, each of the three processes—retort, electrolytic and electrothermic—has its particular field and there are undoubtedly places in the U. S. where the electrothermic process could be profitably applied. Conditions being equal, the electrothermic process may be said to have the advantage over the electrolytic process in the items of power, labor metal recovery, cost of roasting, first cost of plant, and in its adaptability to smaller-scale operations; and over the retort process in the items of reduction fuel, labor, metal recovery, ability to treat low-grade and impure ores, cost of roasting, first cost of plant, and cost of retorts and condensers. C. G. F.

**Making iron from ore by a new electrolytic process.** E. C. KREUTZBERG. *Iron Trade Rev.* **73**, 595-8 (1923); cf. *C. A.* **17**, 1926.—Electrolytic Fe is being made at Millford, Conn. by the *Eustis process*. From an Fe sulfide ore, iron is produced of an av. purity of 99.9%. The ore is first dissolved and reduced to FeCl<sub>2</sub>, this being electrolyzed in a sep. cell away from FeCl<sub>3</sub> and the Fe deposited from it. The S is recovered as a by-product. The consumption of elec. current is about 1 amp. hr. per g. of Fe deposited. The cost of the Fe is about \$50 to \$60 per net ton of finished tubes or sheets after deducting the value of the S, while the capital charges for the plant will probably range from \$10 to \$20 per ton. J. L. WILEY

**Electrolytic zinc plant at Great Falls, Montana.** W. E. MITCHELL AND J. P. COOPER. *Chem. Eng. and Mining Review* **15**, 320-2 (1923).—The problem is to sep. the Zn from an ore high in Fe and Pb. The concentrate is first thoroughly roasted in multiple-hearth furnaces. The ZnO is next leached out with H<sub>2</sub>SO<sub>4</sub>, forming ZnSO<sub>4</sub>, 3 successive leaching operations being necessary to ext. all the Zn. The residue contains all the Au, Ag, and Pb. Filtration is accomplished in continuous vacuum filters. The soln. is purified by agitation with finely divided Zn, which ppts. out the Cu and Cd as a black deposit. After filtering again, the soln. is free of all impurities and is ready for the electrolysis. The electrolytic cells are of wood construction lined with sheet Pb, each being 10'-3" × 2'-10" and 5' deep with 28 anodes made of Pb and 27 cathodes made of Al. The electrodes are spaced 2" apart. A current of 9500 amperes and 3.5 v. is used. The Zn so obtained is melted and cast into marketable slabs. For melting, a coal-fired reverberatory-type furnace is used. Zn so made meets the Am. Soc. of Testing Materials specifications very satisfactorily. E. F. PERKINS

**The use of mercury in the purification of zinc sulfate solutions.** SAMUEL FIELD. *Trans. Am. Electrochem. Soc.* **44**, preprint (1923).—The importance of a pure electrolyte is emphasized, and the purification problem is discussed. Instead of adding Zn dust, finely divided negative metals, such as Zn or Al, are amalgamated in the purification cell. This is done by adding HgSO<sub>4</sub> to the Zn liquors followed by Zn powder or zinc blue. The impurities are eliminated in preference to the H<sub>2</sub> of the acid added. Economy of Zn is thus effected, and the method becomes applicable also for cases in which high acid content would prohibit purification because of high consumption of Zn. Cost estimates are given. CHAS. H. ELDREDGE

**Multiple electrode systems, as applied to current distribution in electroplating baths.** A. H. HEATLEY. *Trans. Am. Electrochem. Soc.* **44**, preprint (1923).—A theory is developed which states that an electrolyte with *n* electrodes is equiv. to  $n(n-1)/2$  conductors connecting each electrode with every other electrode. Corresponding conductance values are detd. by measurements. Equations showing relation between currents, potentials, and differences of potential are given, and are exply. verified

when  $n = 3, 4, 5$ . The relation of these equations to throwing power and polarization (cathode) is shown with actual tests.

**The structure of electrolytic nickel.** V. KOHLSCHÜTTER AND H. SCHÖDL. *Helvetica Chim. Acta* 5, 490-512(1922).—A study is made of the variation in structure of Ni deposited under various conditions, i. e., from various electrolytes, viz.,  $NiCl_2$ ,  $0.01 N HCl$ ;  $NiCl_2$ ,  $NH_4Cl$ ; satd. soln. of  $NiSO_4$ ,  $(NH_4)_2SO_4$ ,  $6H_2O$ ;  $NiSO_4$ ,  $0.5\% H_2BO_3$ ; with and without the introduction of  $CO_2$ ; and with and without superimposed a. c. The contraction tendency of many of the deposits was detd. by means of Vuilleumier's contractometer (C. A. 13, 1050). The contraction tendency of Ni deposits in H-forming solns. is small, but it is increased by the introduction of a  $CO_2$ -adsorption layer on the cathode. In both cases the surface appeared scaly when magnified and brightly metallic to the naked eye. In solns. forming little H, the contraction is much greater and may continue after the electrolysis is stopped. The deposits have a brown tinge and show no peculiar structure under weak magnification. Superimposed a. c. practically eliminates the contraction tendency, except when  $CO_2$  is introduced, in which case the macroscopic and microscopic appearances are like those of the d. c. product. Metallographic examn. shows that the Ni layers are made up of very small particles 0.0014 to 0.0022 mm. in diam., the larger ones occurring more frequently in the a. c. deposits. Apparently the particles in the d. c. deposits lie farther apart after their contraction than those in the a. c. products. Thus the immediate depositing medium at the cathode is the important factor governing the spontaneous structure change in the deposit. In thick deposits no marked difference in structure is to be found between a. c. and d. c. products, except on the surface. Thus it appears that the deposits with high contraction tendency are first thrown down as very small, highly dispersed particles, which later unite to form larger aggregates, whereas the non-contracting deposits, because of the special conditions at their place of formation, consist primarily of the larger particles. The d. c. deposits are brittle but those from superimposed a. c. are flexible, even though the latter may have a considerable contraction tendency. Thus the brittleness does not appear to have a direct connection with the contraction. However, it appears that H causes the brittleness, only a very small amt. being necessary.

C. C. VAN VOORHIS

**The effect of superimposed alternating current on the depositing and dissolving potentials of nickel.** V. KOHLSCHÜTTER AND H. SCHÖDL. *Helvetica Chim. Acta* 5, 593-609(1922).—Potential measurements were made in connection with the investigation of the structure of Ni deposits (see preceding abstract). Several tables show the electrode potentials at frequent intervals during deposition and dissolution, which usually were continued for 30 min. Superimposed a. c. lowered both the depositing and the dissolving potentials between 0.1 and 0.5 v. Apparently H is the chief factor in these polarization effects also.

C. C. VAN VOORHIS

**Some relations between the microstructure of metal surfaces and electrodeposits made thereon.** A. KENNETH GRAHAM. *Trans. Am. Electrochem. Soc.* 44, preprint (1923).—A study is made of the effect of base metal structure on the structure of the electrodeposit. With various current densities, Cu was deposited on annealed and cold-rolled Cu sheet, on buffed Cu sheet, cold rolled Cu rod, on annealed sheet brass and on Ni. Reproduction is defined as a continuation in the deposit of the structure of the base metal. Conclusions are that reproduction depends not so much on preliminary cleaning as on the structure of the base. Cathodes with large crystals cause reproduction in the deposit to a marked degree of penetration before the typical columnar structure of the electrodeposit starts. Without well formed crystals on the base a new growth does not necessarily start, but apparently surface crystals are reproduced whatever they may be, with but small penetration however. Deposits of Ni or of Cu on Ni gave uncertain results due to etching difficulties.

CHAS. H. ELDRIDGE

**The crystalline form of electrodeposited metals.** WM. BLUM AND H. S. RAWDON. *Trans. Am. Electrochem. Soc.* 44, preprint(1923).—A simple theory of the mechanism of crystal formation in electrodeposition is outlined, according to which: (a) The cathode discharge of metal ions and the formation of crystals constitute one and the same process. (b) Any given ion is discharged at the point at which the lowest discharge potential is required. (c) The discharge potential is a function of the soln. pressure and the "effective" metal ion concn. adjacent to it. (d) The single potential and soln. pressure of a metal are the resultant of the "primary single potential," which is defined in terms of the soln. pressure of a single unoriented atom, and the "orientation potential," which is a measure of the diminution in soln. pressure and corresponding algebraic increase in single potential caused by the arrangement or orientation of the adjacent metal atoms. (e) A higher potential is required to discharge an ion in a position



unrelated to those of previously discharged atoms (that is, to form a nucleus), than upon an existing crystal, and similarly a higher potential is required to discharge in ion upon a small crystal than upon a large one. Typical structures of electrodeposits are classified into 3 major groups, viz: Group I. All (or practically all) of the initial nuclei continue to grow. Group II. Only a part of the initial nuclei continues to grow. Group III. None of the initial nuclei continues to grow. The factors which det. the character of the crystals are discussed, and the direction of the change produced by any change in operating conditions is predicted and discussed. Diagrams and micrographs illustrate typical structures. The important generalization is made that one may expect to produce upon the same base metal similar cryst. forms *whenever the cathode potential is the same*, whether secured with a low current density in a dil. soln., with correspondingly higher c. d. in more concd. soln., or with still higher c. d.'s in agitated solns., or by any other means, *provided the potential gradients through the soln. are the same in each case.*

CHAS. H. ELDRIDGE

**Action of barium chloride on sulfate in fused salts.** H. E. BATSFORD. *Ind. Eng. Chem.* 15, 1044(1923).—By expts. in the regular operation of the electrolytic cell contg. NaCl and CaCl<sub>2</sub> in which a small amt. of BaCl<sub>2</sub> was present it was proved that BaCl<sub>2</sub> did not change the f. p., and in molten mixtures acted as purgative, pptg. quant. the sulfate present as impurity in the salts.

HOWARD E. BATSFORD

**Consumption of sulfuric acid in the lead storage battery.** H. CASSEL AND F. TÖDT. *Z. angew. Chem.* 36, 227-8(1923).—The Rayleigh liquid interferometer (Zeiss type) was employed to test Fery's theory that the Pb storage battery reaction was  $\text{Pb}_2\text{O}_{3+1} + \text{Pb} + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + x\text{PbO}_2 + \text{H}_2\text{O}$ . Careful tests with smooth Pb plates, on the basic assumption that as many moles of acid disappear as moles of water are generated, led to the conclusion that the sulfate reaction (Gladstone and Tribe) was correct and that the discrepancies which had cast doubt on its correctness were due solely to the extraordinary slowness of the equalization of acid between the pore contents and the external soln. The results of the tests are reported in detail in tabular form.

GEORGE C. O. HAAS

**The charging of small accumulators.** ANON. *Beama* 13, 262(1923). C. G. F.  
**The manufacture of chemicals by electrolysis. I and II. The electrolysis of alkali chlorides.** ALBERT CLARKE. *Beama* 12, 165-72, 348-55(1923). III. Organic compounds. *Ibid* 13, 246-54.—A review. C. G. F.

**Stray current electrolysis.** E. R. SHEPARD. *J. Am. Water Works Assoc.* 10, 603-11(1923).—Damages from electrolysis are decreasing. Present research is along the line of its mitigation as well as the effect of chem. agencies possibly responsible. Stray current action being more rapid may produce black or magnetic oxides, while chem. rusting usually produces the red oxide.

D. K. FRENCH

**The calibration of oil-immersed water-cooled standard low resistances.** B. G. CHURCHER. *Electrician* 91, 360-1(1923). C. G. F.

#### An electric furnace for vitreous enameling (SCHUIJER) 19.

**Storage battery.** E. A. STALLINGS. U. S. 1,469,119, Sept. 25. Structural features of an escape device for gas and splash from the battery.

**Storage battery.** L. L. JONES. U. S. 1,469,015, Sept. 25. Structural features.

**Electrolyte for storage batteries.** L. E. BROWNELL. U. S. 1,468,957, Sept. 25. A compn. for use instead of ordinary H<sub>2</sub>SO<sub>4</sub> electrolyte is formed of H<sub>2</sub>SO<sub>4</sub> 20 gals., H<sub>2</sub>O 80 gals., alum 25 lbs., glycerol 33 lbs. and MgSO<sub>4</sub> 50 lbs. Cf. C. A. 17, 2239.

**Separator for storage batteries.** H. A. YARNELL. U. S. 1,470,518, Oct. 9. Structural features.

**Water-feeding device for storage batteries.** J. D. SARTAKOFF. U. S. 1,469,963, Oct. 9.

**Electric battery terminals.** A. FRETSCHEL. U. S. 1,470,433, Oct. 9. Structural features.

**Graphitizing electrodes.** E. SZARVASY. U. S. 1,470,300, Oct. 9. C electrodes are graphitized by heating them in CH<sub>4</sub> at a temp. at which the CH<sub>4</sub> decomposes.

**Cathode for electrolytic refining of copper or other metals.** C. H. SCHUH. U. S. 1,468,838, Sept. 25. Plate cathodes of Al or other "film-forming" metals are made with chamfered edges to fit a frame of rubber or other non-conducting material.

**Anode for production of persalts.** O. LIEBKNECHT. U. S. 1,470,577, Oct. 9. Anodes adapted for use in electrolytic production of perborates or other persalts are formed of Pt foil or gauze with a reinforcing frame of metallic Zn.

**Apparatus for electrical precipitation of suspended particles from gases.** E. MÖLLER and W. HOSS. U. S. 1,469,275, Oct. 2.

**Electric crucible furnace.** M. DE ROHOU. U. S. 1,470,195, Oct. 9. A crucible comprising oxides of Zr, Yt and Er is first heated to a conducting temp. and then further heated by direct passage of a high-voltage current. The furnace is adapted for fusing  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ .

**Electric furnace adapted for reducing tungsten.** W. P. BLECKER. U. S. 1,469,033, Sept. 25.

**Melting metals in an electric furnace.** I. RENNERFELT. U. S. 1,469,817, Oct. 9. A carefully insulated elec. furnace is gradually charged with Fe or steel or other metal during a period of nearly 24 hrs. and the metal is caused to melt by supplying elec. power sufficient to cover the loss of heat from the furnace and furnish additional heat for slowly melting the metal in the quantity intended to be discharged every 24 hrs. This mode of operation is adapted for economical melting in foundry casting.

**Electroplating apparatus.** VAN WINKLE TODD. U. S. 1,468,764, Sept. 25. Articles under treatment may be moved longitudinally along a channel shaped cathode bar upon the vertical flanges of which the articles are supported.

**Commutator composition.** J. E. FISHER. U. S. 1,469,039, Sept. 25. A spark-preventing compn. for use on commutators is formed of an asphaltic oil, an oil with a paraffinic base, kerosene and oil of wintergreen.

**Composite electric contact material.** C. A. LAISE and O. C. HOLLOPETER. U. S. 1,469,043, Sept. 25. Joining material such as Cu and  $\text{NH}_4$  chloroplatinate is placed between a backing of steel or other base metal and a face plate of Pt or other refractory metal and a combined heating unit and holder formed of dense Cr-Ni alloy is used for heating the backing and facing together to a welding temp. in an inert atm., e. g.,  $\text{NH}_3$  or a mixt. of N and H.

## 5—PHOTOGRAPHY

C. E. K. MEES

**Photographic intensity of flash-light materials.** EMERY HUSE. *J. Franklin Inst.* 196, 391-5(1923).—The photographic intensity of the flash powder is greater when detd. on ordinary (blue-sensitive) materials than when orthochromatic and panchromatic materials are used. The reverse is true of Mg powder and ribbon. The presence in the flash powder of accelerators and of other metals in addition to Mg tends to produce a greater proportion of radiation in the region of shorter wave lengths, and a bluer light.

**The dyes used in photography.** D. S. MUSGILLO and C. W. GIBBS. *Am. Dyestuff Reporter* 12, 47-8(1923).—Attention is directed to the properties of well-known dyes and their important application to optical filters, sensitizers and desensitizers, coloring of elec. lamp bulbs, manuf. of safe-lights, tinting, toning and hand coloring of transparencies and staining of microscopical samples. The review is intended to direct the attention of dye manufacturers and salesmen to the field and application of such dyes in photography.

**Absorption of sodium thiosulfate by photographic paper.** A. CHARRIGU. *Compt. rend.* 177, 482-4(1923).—The retention of "hypo,"  $\text{Na}_2\text{S}_2\text{O}_3$ , by photographic paper was shown to be an adsorption phenomena by means of analyses of the paper and wash water at various stages of washing. It was, also, found that the  $\text{Na}_2\text{S}_2\text{O}_3$  could be displaced more readily by washing in a soln. of alkali carbonate or phosphate than by water.

C. E. K. MEES

**Influence of adsorbed substances on the spectral sensitiveness of silver bromide (FRANKENBURGER) 3. Action of light on silver bromide (STRÖMBERG) 3.**

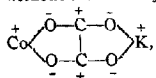
**Color photography.** J. G. CAPTAPP. U. S. 1,469,811, Oct. 9. Component Ag images are made and severally transformed into complementary dye images. The Ag images are formed with different density and contrast and these differences are compensated for in the transformations.

**Photographic development gage.** W. F. HERZBERG. U. S. 1,469,415, Oct. 2. Latent indexes are provided on the margin of plates or films which become visible consecutively upon continued development.

## 6—INORGANIC CHEMISTRY

A. R. MIDDLETON

**Chelate coordination.** J. D. MAIN SMITH. *Chemistry and Industry* 42, 847-50 (1923).—Polemic, criticizing Lowry's differentiating two types of coordination, centric and cyclic (C. A. 17, 3291). A chelate group is defined as "a linked system of atoms which in combination with another atom, completes a cyclic system." Since all cyclic groups have centric atoms at their reacting ends, S. does not consider that "fundamentally differing types of coordination" exist," and points out that differences of stability, according to Werner, are due to differences in intensity and not in type of coordination. Ethylenediamine, contrary to L., is held to be an active chelate group forming more stable compounds than  $\text{NH}_3$ . Exception is also taken to L.'s statement that ring-formation does not decisively promote stability, and comparison is made of the unstable ferrous amines and the stable ferrous  $\alpha, \alpha$ -dipyridyl deriv. S. objects to the introduction of elec. concepts in consideration of Werner's theory, which was developed without them. Objection is made to the coordination of an alkali metal in L.'s formula,



with its tervalent C; and finally it is pointed out that metals of

the extended transition-series (e. g., Fe) occasionally have no "centric" properties, as stated by L., and other metals often have "centric" properties highly developed (Be, B, Al, Si, N, O, F).

A. W. KENNEY

**The system  $\text{BaS}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ .** MISS W. C. DE BAAT. *Rec. trav. chim.* 42, 643-6 (1923).—Several double dithionates of these 2 salts have been described. de B. has studied this system at 30°, 20.1° and 12°. The results given in tables and graphs show that at these temps. the 2 salts  $\text{BaS}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  are the only solids sepd. and that they do not sep. either as a double salt or as mixed crystals. The supposed double salts previously reported were probably conglomerates of 2 hydrates.

R. J. WITZEMANN

**The systems  $\text{KCl-MgCl}_2\text{-H}_2\text{O}$  and  $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$ .** H. KRITEL. *Kali* 17, 248-51, 261-5 (1923).—In support of early observations of van't Hoff it was found that the invariable equil. points of the systems  $\text{KCl-MgCl}_2\text{-H}_2\text{O}$  and  $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$  do not lend themselves to rectilinear combination. In the system  $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$  the individual mols. combine to form a complex similar to carnallite. Under the conditions of the expts. this "Na carnallite" did not exist in the solid phase. In the presence of solns. contg. considerable  $\text{MgCl}_2$  carnallite dissolves with the formation of highly supersatd. solns.

K. D. JACOB

**Complex formation in lead nitrate solutions. I. Ternary systems lead nitrate-sodium nitrate-water, and lead nitrate-potassium nitrate-water.** S. GLASSTONE AND H. N. SAUNDERS. *J. Chem. Soc.* 123, 2134-40 (1923).—The ternary systems were investigated completely at 25° and 50° and partially at 0° and 100°. The liquid and wet solid phases were analyzed; the results were plotted on the triangular diagram and extrapolated to the dry solid phase by the method of Schreinemakers.  $\text{NaNO}_3$  decreases the soly. of  $\text{Pb}(\text{NO}_3)_2$ , the effect increasing with rising temp. The decrease in soly. becomes smaller as the amt. of  $\text{NaNO}_3$  increases.  $\text{KNO}_3$  always appears to increase the soly. of  $\text{Pb}(\text{NO}_3)_2$ , but the effect decreases greatly with increasing temp. The difference in behavior of the two alk. nitrates is ascribed to difference in degree of complex formation and of hydration, factors which act in opposite direction. Both may be influenced by temp. That the activity of water is much less in  $\text{NaNO}_3$  than in  $\text{KNO}_3$  solns. is shown by the fact that the latter evaps. much more rapidly.

A. R. M.

**Hydrates of potassium and lithium cyanoplatinites and the system potassium cyanoplatinite-lithium cyanoplatinite-water.** H. TERRY AND V. G. JOLLY. *J. Chem. Soc.* 123, 2217-22 (1923).—Solubilities were detd. at frequent intervals between 0° and 100°. Some values (g. anhyd. salt in 100 g. water) are: K salt, 0.10° 11.60; 20.05° 33.83; 45° 95.43; 95° 210.9. Li salt, 0° 105.0; 25° 144.7; 89.8° 238.7. For the K salt indications (soly. being plotted against temp.) were obtained for the hydrates 1-2, 3-5, 5 $\text{H}_2\text{O}$ ; dilatometric methods gave transition temps. 13.35° (3 $\text{H}_2\text{O}$ ); 52.4° (2 $\text{H}_2\text{O}$ ); 74.4° (1 $\text{H}_2\text{O}$ ) nearly identical with those from the soly.-temp. curve. For the Li salt transition pts. were shown at 26, 38, 46 and 69° by the dilatometric method and at 29.5°, 39.5°, 49° and 72° by the soly.-temp. curve. At ordinary temp. the 5-hydrate seps.; dehydrating moist crystals in dry air made a 4-hydrate certain; on rehydration in air of the

dehydrated salt, 3 mols.  $H_2O$  are taken up quickly followed more slowly by full hydration. From mixed soln. a double salt,  $LiKPt(CN)_2H_2O$ , seps. until concn. of K salt in the liquid becomes 38% when the 3 hydrate of the K salt seps. The double salt is ruby-red with characteristic blue shimmer; on dehydration it gives a yellow solid which rapidly rehydrates to the original 2-hydrate. A small amt. of this double salt imparts a red color to a mass of the Li salt. This explains discrepancies in descriptions of the Li salt. A. R. M.

**System ferric oxide-phosphoric acid-water.** A new phosphate. S. R. CARTER AND N. H. HARTSHORNE. *J. Chem. Soc.* 123, 2223-33(1923).—The system was studied at 25° and 70°. At 25° the work of previous investigators on the neutral ferric phosphates could be coordinated. It is concluded as probable that at the lowest acid concns. a compd.,  $Fe_2O_3 \cdot P_2O_5 \cdot xH_2O$ , is stable which adsorbs  $H_3PO_4$  from the mother liquor and is a true ferric phosphate. At higher concns. this changes to a compd.,  $Fe_2O_3 \cdot P_2O_5 \cdot 5H_2O$ , which has no adsorptive power and is probably a ferric ferriphosphate. At 70° is shown, in addn. to the above phases, the previously known compds.,  $Fe_2O_3 \cdot 2P_2O_5 \cdot 8H_2O$  and  $Fe_2O_3 \cdot 3P_2O_5 \cdot 5.6H_2O$  and a new compd., to which the formula  $Fe_2O_3 \cdot 3P_2O_5 \cdot 10H_2O$  is assigned. A. R. M.

**Reaction between phosphorous acid and iodine.** A. D. MITCHELL. *J. Chem. Soc.* 123, 2241-54(1923); cf. *C. A.* 14, 3353, 15, 621, 3652; 16, 3822; 17, 2214. As the reactions of  $H_3PO_3$  had been found explicable on the basis of its tautomerism, a detailed study of  $H_3PO_3$  was undertaken. Although the reaction with I is very complicated strong evidence has been found for similar tautomerism. The reaction involves iodine both as  $I_2$  and as  $I_3^-$  and a second form of  $H_3PO_3$  formed reversibly from the first.  $I_2 + H_2O \rightleftharpoons HI + HOI$   $I_3^- + H_2O \rightleftharpoons I_2 + OH^-$   
It is represented as  $H_3PO_3 + 2HI \rightleftharpoons H_3PO_3 \cdot 2HI \rightleftharpoons H_3PO_3 + 2HI + 3I^-$   
(normal form) (second form)

+  $3I^-$ .  $H^-$  ion represses the left hand reaction and accelerates the right hand one but this acceleration is probably only indirect and due to acceleration of the equil. between the two forms of  $H_3PO_3$ . The mechanism of the repressing effect has not yet been elucidated. Finality is not claimed as to details and directions are indicated in which these may have to be modified or amplified. It is regarded as certain that any explanation must be based on the existence of a second form of  $H_3PO_3$ . A large amt. of exptl. material is presented. A. R. M.

**Equilibrium in the systems, nickel chloride, cobalt chloride, cupric chloride-hydrochloric acid-water.** H. W. FOOTE. *J. Am. Chem. Soc.* 45, 663-7(1923). Data in tabulated and graphical form are given of the soly. at 0° (and for  $CuCl_2$  at 25° also) of  $NiCl_2$ ,  $CoCl_2$  and  $CuCl_2$  in the presence of increasing amts. of HCl. The solid phases in equil. with the solns. were also studied.  $CuCl_2$  gave a dihydrate only;  $NiCl_2$  gave a tetrahydrate and dihydrate besides the ordinary hexahydrate, whereas  $CoCl_2$  gave, besides the hexahydrate, only a dihydrate. The soly. of all salts decreased rapid with increase in HCl content, owing to the common ion. The subsequent increase due to complex formation was most marked with  $CuCl_2$ , which deposited an addn. product, the compd.  $HCl \cdot CuCl_2 \cdot 3H_2O$ , at 0°. It is suggested that, based on the difference in soly. of Ni and Co salts in concd. HCl, a method be developed for *freeing Ni salts from small amts. of Co salts*. C. C. DAVIS

**The properties of ammonium nitrate. VI. The reciprocal salt pair ammonium nitrate and potassium sulfate.** E. P. PERMAN AND W. M. J. HOWELLS. *J. Chem. Soc.* 123, 2128-34(1923); cf. *C. A.* 17, 2398.—The system,  $NH_4NO_3$  plus  $K_2SO_4$  studied by means of f. p. curves, gives evidence of 3 sets of mixed crystals,  $NH_4NO_3$  and  $KNO_3$ ;  $NH_4NO_3$  and  $(NH_4)_2SO_4$ ; and  $(NH_4)_2SO_4$  and  $K_2SO_4$ . A ternary point exists at 156.5°, at which these 3 pairs are in equil. The f. p. of  $NH_4NO_3$  itself is raised steadily by the addn. of  $(NH_4)_2SO_4$ . Complete f. p. data are given. A. W. KENNEY

**Dissociation of complex cyanides.** G. J. BURROWS. *J. Chem. Soc.* 123, 2026-9(1923).—Cond. measurements have been made with solns. of  $K_3Fe(CN)_6$ ,  $Na_3Fe(CN)_6$ ,  $K_3Co(CN)_6$ ,  $K_3Cr(CN)_6$ , and  $K_3Cr(CN)_6$ . (Temp. not given.) The values of  $\mu$  for  $K_3Fe(CN)_6$  and  $K_3Co(CN)_6$  are best interpreted on the assumption that these salts dissociate as follows: the former into  $4K^+$  ions and one quadrivalent anion, the latter into  $3K^+$  ions and one trivalent anion. H. JERMAIN CREIGHTON

**The equilibrium between lead iodide and ammonium iodides in aqueous solution.** N. DEMASSEIUX. *Compt. rend.* 177, 51-4(1923).—Tabulated data and equil. diagrams are given for the systems  $PbI_2-KI-H_2O$  and  $PbI_2-NH_4I-H_2O$ . The results indicate the formation of the double salt  $PbI_2 \cdot KI \cdot 2H_2O$  and the double salt  $PbI_2 \cdot NH_4I \cdot 2H_2O$  (cf. *Am. Chem. J.* 18, 290(1896); *Z. anorg. Chem.* 3, 195(1893)) but of no other compds. described by past investigators (*Ann. chim. phys.* 34, 366(1827);

[5] 29, 289(1883); [7] 12, 374(1897); Ditte, *Ibid* [5] 24 (1881); *Compt. rend.* 20, 1180; *Z. physik. Chem.* 10, 477(1892); *J. Chem. Soc.* 63, 540; *Chem. News* 67, 157(1893); *Bull. soc. chim.* 1, 346(1897); Balcom, Abegg, *Handbuch der anorg. Chem.* Vol. 3(2), 667). C. C. DAVIS

Conversion of calcium phosphates into chloro derivatives of phosphorus by means of sulfur chloride. P. P. BUDNIKOV AND E. A. SHILOV. *J. Soc. Chem. Ind.* 42, 378T (1923); cf. C. A. 17, 3754.— $S_2Cl_2$  was led through pure Ca ortho- or meta-phosphate mixed with  $SiO_2$  or coal, or both, at 350–1000°. With  $Ca_3(PO_4)_2$  the reaction is very slow even at 1000°, about 9% conversion being obtained with a strong current of  $S_2Cl_2$  in 1 hr. With  $Ca(PO_3)_2$  at the same temp. 19.5% conversion was obtained in 1 hr. without  $SiO_2$  or C, 90.5% with  $SiO_2$  and 99% with  $SiO_2$  and C. In this last expt. the amts. used were:  $Ca(PO_3)_2$  2 g.,  $SiO_2$  0.6 g., coal 2 g.,  $S_2Cl_2$  100 g. With the same amts. conversion was 16% in 1 hr. at 800° and practically nil at 600°. The liquid products consisted chiefly of  $PCl_3$  and  $PSCl_3$ ;  $SO_2$ , S, and  $SiCl_4$  also were formed.

A. R. MIDDLETON

The ternary system sulfur-selenium-tellurium (LOSANA) 2.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

An application of the vacuum tube to chemistry. D. F. CALHANE AND R. E. CUSHING. *Ind. Eng. Chem.* 15, 1118–20(1923).—An interesting electrometric method for detg. 0.01–0.0025 *N* chloride content by titration with  $AgNO_3$ . A 3-electrode tube, widely used in radio work, connected with a second or plate battery and a concn. cell are used in the analysis. In the known limb of this cell is a Ag wire dipping into 0.1 *N*  $K_2CrO_4$  soln. satd. with  $Ag_2CrO_4$  and this is connected by a siphon of 0.1 *N*  $KNO_3$  soln. made solid with agar. In the other arm of the cell is a silver wire dipping into the chloride soln. which is to be titrated with 0.01 *N*  $AgNO_3$ . This cell is connected with the grid circuit of the 3-electrode tube so that a change in the negative potential of the grid is produced as the titration proceeds. The end-point is reached when no further change is produced. W. T. H.

Qualitative and quantitative chemical analysis by means of X-rays. D. COSTER. *Z. Elektrochem.* 29, 344–8(1923).—An address. H. JERMAIN CREIGHTON

Recent applications of electrotitrimetry to chemical analysis. JEAN BARBAUDY. *Technique moderne* 15, 545–53(1923).—A review of the principles underlying  $p_H$  detn. and its applications in analytical chemistry, illustrated by typical examples (acidimetry, alkalimetry, detn. of HCN, Cl, Br and I by pptn. with Ag, oxidation and reduction).

A. PAINNEAU-COUTURE

The quantitative treatment of the metals of the ammonium sulfide group. G. LUFF. *Z. anal. Chem.* 63, 32–9(1923).—Expts. in segg. trivalent Fe and Al from bivalent Mn, Zn, Co and Ni cations show that a double pptn. with  $NH_4OH$  in the presence of  $NH_4Cl$  is not as a rule satisfactory but far better results are obtained if pyridine is substituted for the first pptn. W. T. H.

Systematic procedure for the detection and separation of acids. Z. KARAOGLANOV AND M. DIMITROV. *Z. anal. Chem.* 63, 1–10(1923).—The acids are grouped as follows according to their volatility and behavior toward precipitants. I. Easily volatile from AcOH soln.:  $H_2CO_3$ , HCN,  $H_2SO_3$ ,  $H_2S_2O_3$ ,  $H_2S$ ,  $HNO_2$  and  $HClO$ . II. Acids not pptd. by  $Ba(OAc)_2$  in acid or neutral soln. or by  $AgNO_3$  in  $HNO_3$  soln.:  $H_3PO_4$  and  $HNO_3$ . III. Completely pptd. in AcOH soln. by a mixt. of  $Ba(OAc)_2$  and  $Ca(OAc)_2$ :  $H_2SO_4$ ,  $H_2SiF_6$ ,  $H_2CrO_4$ , HF,  $H_2C_2O_4$ ,  $HIO_3$  and  $H_2C_2H_3O_4$ . IV. Acids whose Ba salts and Ca salts are insol. in water:  $H_3PO_4$ ,  $H_2AsO_4$  and  $H_2SiO_4$ . V. Acids whose Pb salts are insol. in water:  $H_2Fe(CN)_6$ ,  $H_2AsO_4$  and  $H_2C_2H_3O_4$ . VI. Acids pptd. by Pb salts in  $NH_4$  soln.:  $H_2Fe(CN)_6$  and  $H_2AsO_4$ . VII. Acids pptd. by  $AgNO_3$  in  $HNO_3$  soln.: HCl, HBr, and HCNS. VIII. Acids not pptd. by Ba, Ca, Pb and Ag salts:  $HClO_4$ ,  $HClO_3$  and  $HBrO_3$ . The above classification includes all the common acids except AcOH, which is an indispensable reagent in the scheme and must be tested for at the start. Prep. the soln. free from heavy metals by the customary methods. Test for AcOH by attempting to form ethyl acetate or cacodyl. Place 20–50 cc. of the neutral soln. in a flask, add 5–10 cc. of 2 *N* AcOH, pass air or  $H_2$  through the flask and test the escaping gas with  $AgNO_3$ ,  $Ba(OH)_2$  and KI-starch solns. If no test is obtained and the soln. does not become turbid on adding concd.  $H_2SO_4$  to the contents of the flask then no acids of Group I are present.  $H_2CO_3$  causes turbidity with  $Ba(OH)_2$  soln. but

does not decolorize starch iodide soln.  $\text{H}_2\text{SO}_4$  decolorizes starch iodide but gives no ppt. with  $\text{AgNO}_3\text{-HNO}_3$  soln.  $\text{HCN}$  gives a ppt. with  $\text{AgNO}_3\text{-HNO}_3$  and the characteristic Prussian blue reaction.  $\text{H}_2\text{S}$  blackens the  $\text{AgNO}_3$  soln., has a characteristic odor and blackens the  $\text{AcOH}$  soln. of  $\text{Pb}(\text{OAc})_2$ .  $\text{H}_2\text{S}_2\text{O}_8$  is characterized by causing S to ppt. when concd.  $\text{H}_2\text{SO}_4$  is added to the soln. If  $\text{HNO}_3$  is present, the gas stream colors KI-starch blue, does not decolorize indigo soln., turns the Griess reagent red and that of Zlatarov blue.  $\text{HClO}$  causes a turbidity with  $\text{AgNO}_3$  soln., gives a blue with KI-starch and decolorizes indigo soln. To detect the acids of Group II, remove all acids of Group I and test a part of the soln. for  $\text{HNO}_3$  with diphenylamine soln. and after reduction with Zn with Nessler's reagent. Test for  $\text{H}_2\text{BO}_3$  by the flame test or with turmeric. The scheme does not provide for the sepn. and removal of these acids. To the soln. add Ba and then Ca acetate solns. until no further pptn. takes place filter and test the ppt. for members of Group III. Treat the ppt. with dil.  $\text{HNO}_3$ . The heat test on the residue shows whether any  $\text{H}_2\text{SO}_4$  is present. Test for  $\text{H}_2\text{SiF}_6$  by treating some of the ppt. with concd.  $\text{H}_2\text{SO}_4$  and see if the escaping gas turns water turbid. Test for  $\text{HIO}_3$  with  $\text{HCl}$ , starch and a little Zn to see if  $\text{I}_2$  is liberated upon reduction. Test the  $\text{HNO}_3$  soln. of the Ba and Ca ppt. (in the absence of  $\text{H}_2\text{C}_2\text{O}_4$ ) for HF and  $\text{H}_2\text{C}_2\text{O}_4$  by forming the Ba or Ca salt and treating with  $\text{H}_2\text{SO}_4$  and powdered glass to see if  $\text{H}_2\text{SiF}_6$  is evolved; pass the gas through  $\text{BaCl}_2$  soln. to remove  $\text{H}_2\text{SiF}_6$  and then through  $\text{Ba}(\text{OH})_2$  soln. to see if  $\text{CO}_2$  is present from  $\text{H}_2\text{C}_2\text{O}_4$ . If  $\text{H}_2\text{CrO}_4$  is present, a green residue is obtained which dissolves in water and gives tests for trivalent Cr. If considerable  $\text{H}_2\text{C}_2\text{H}_3\text{O}_4$  is present it appears chiefly in Group III. In that case ppt.  $\text{BaSO}_4$ ,  $\text{CaC}_2\text{O}_4$  and  $\text{CaF}_2$  in dil.  $\text{AcOH}$  soln. and in the filtrate test for  $\text{HIO}_3$  with  $\text{Na}_2\text{S}_2\text{O}_8$  and starch, for  $\text{H}_2\text{CrO}_4$  with  $\text{H}_2\text{O}_2$  and for  $\text{H}_2\text{C}_2\text{H}_3\text{O}_4$  with  $\text{KMnO}_4$  or by the Ag mirror test. In the filtrate from Group III, ppt. Ba salts of  $\text{H}_2\text{PO}_4$ ,  $\text{H}_2\text{AsO}_4$  and  $\text{H}_2\text{SiO}_4$  with  $\text{NH}_4\text{OH}$  and  $\text{Ba}(\text{OAc})_2$ . Test for the first acid with molybdate, reduce with sulfite and test for As with  $\text{H}_2\text{S}$  and for silicic acid in the usual way. Dil. the filtrate from Group IV and ppt. with  $\text{Pb}(\text{OAc})_2$  in a neutral soln. Boil with water and  $\text{AcOH}$ . If HI is present yellow  $\text{PbI}_2$  will be noticeable. Remove Pb as  $\text{PbSO}_4$  and test for  $\text{H}_2\text{AsO}_4$  with  $\text{H}_2\text{S}$ . Test for  $\text{H}_2\text{C}_2\text{H}_3\text{O}_4$  by the Ag mirror test and for  $\text{H}_2\text{Fe}(\text{CN})_6$  by the blue color that gradually develops on adding  $\text{FeCl}_3$  to the ppt. of the Pb salt which was insol. in  $\text{AcOH}$ . Test for group VI by adding considerable  $\text{NH}_4\text{OH}$  to the filtrate from Group V. Boil and filter while hot. Under these conditions  $\text{H}_2\text{Fe}(\text{CN})_6$  is reduced and can be detected in the Pb ppt. by the Prussian blue test. Test for  $\text{H}_2\text{AsO}_4$  as above. In the filtrate from Group VI, first test for  $\text{HCNS}$  with  $\text{FeCl}_3$  in a part of the soln. The sepn. of the halogen acids takes place along conventional lines after pptn. with  $\text{AgNO}_3$ . To the filtrate from group VI, add  $\text{H}_2\text{SO}_4$  to remove Pb ions. Add  $\text{AgNO}_3$  and Zn.  $\text{AgCl}$  and  $\text{AgBr}$  are formed if  $\text{HClO}_3$  or  $\text{HBrO}_3$  was present. Remove Ag and Zn ions with  $\text{KOH}$ , boil the filtrate with  $\text{FeSO}_4$ , filter, boil with  $\text{HNO}_3$  and test for Cl ions with  $\text{AgNO}_3$  to see if  $\text{HClO}_4$  was present.

W. T. H.

**The estimation of chromium in nickel-chrome alloys.** "METT." *Chem. Age* (London) 9, 364(1923).—Heat 0.2–1 g. of alloy in a Ni crucible with 10 g.  $\text{Na}_2\text{O}_2$ . Ext. the  $\text{Na}_2\text{CrO}_4$  with water, make acid with  $\text{HNO}_3$ , neutralize with  $\text{NH}_4\text{OH}$  and then acid with  $\text{AcOH}$ . Ppt.  $\text{PbCrO}_4$ , filter, dissolve in 2 N  $\text{H}_2\text{SO}_4$  and det. Cr volumetrically with  $\text{FeSO}_4$  soln. and  $\text{KMnO}_4$  in the usual way.

W. T. H.

**The determination of chromium in the presence of organic matter.** GEORGE GRÄSSER. *Z. Leder-Geberet-Chem.* 2, 185–8(1923).—Several methods for the destruction of org. matter in chrome liquors were tried. It was found that oxidation with either  $\text{KClO}_3$  or fusion with  $\text{KNO}_3$  and subsequent titration with  $\text{Na}_2\text{S}_2\text{O}_5$  gave good checks with the gravimetric detn. of Cr. Where  $\text{KMnO}_4$  was used, variable results were obtained.

ERWIN J. KERN

**Simplified determination of arsenic.** POUSSIEUX. *Ann. chim. anal. chim. appl.* 5, 263–7(1923).—The method is similar in principle to that recommended by COPPIN for the detn. of  $\text{H}_2\text{PO}_4$ . If a soln. of  $\text{Na}_2\text{MoO}_4$  in dil.  $\text{HNO}_3$  is mixed with pure ether and then treated with  $\text{H}_2\text{AsO}_4$ , 3 layers of liquid result. The bottom layer consists of an oily, yellowish liquid contg. As and Mo; the middle layer is an aq. soln. contg. the excess of  $\text{Na}_2\text{MoO}_4$  and the top layer consists of the excess ether. If the reaction takes place in a centrifuge tube graduated at the bottom, which is narrower than the rest of the tube, the quantity of As can be detd. by the depth of yellow liquid. It is necessary, however, to apply a correction for the soly. of the As compd. in the other 2 liquids. By this method of analysis good results are easily obtained in the analysis of tetrahydrite, pyrite and similar minerals contg. more than traces of As and no P. In the analysis it is recommended to use 25 cc. of soln. contg. 2.9 to 25 mg. of As, which should

be added to a mixt. of 65 cc.  $\text{Na}_2\text{MoO}_4$  soln. (100 g.  $\text{MoO}_3$  suspended in hot water, neutralized with  $\text{Na}_2\text{CO}_3$ , poured into 700 cc. of 6  $N$   $\text{HNO}_3$  and diluted to 1 l.) and 85 cc. of ether.

**Estimation of small quantities of calcium.** P. P. LAIDLAW AND W. W. PAYNE. *Biochem. J.* 16, 494-8(1922).—The method described is suitable for estg. Ca in amts. of the order of 0.1 mg., and gives results accurate to about 0.002 mg. First ppt. the Ca as oxalate (in the case of blood serum, this may be done directly from the serum without previous ashing). After sepn., dissolve the ppt. in  $\text{HCl}$  and reppt. the Ca in the form of Ca alizarinate by the addn. of excess of alizarin in alc. soln., and, after warming, of a few drops of strong  $\text{NH}_4\text{OH}$ . When cryst., collect the ppt. in a Gooch crucible, wash with dil.  $\text{NH}_4\text{OH}$  and decompose with a soln. of oxalic acid in 50% alc. Dissolve the liberated alizarin in 95% alc., make just alk. with  $\text{NH}_4\text{OH}$ , and est. colorimetrically by comparison with a standard soln. of  $\text{NH}_4$  alizarinate.

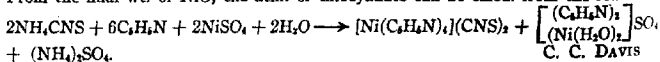
**Reduction of bismuth by dextrose.** H. COUSIN. *J. pharm. chim.* 23, 179-81 (1923).—The black ppt. obtained from a sol. or insol. Bi salt, by warming on a water bath with dextrose in presence of  $\text{NaOH}$ , approaches 100% Bi (above 97.87%) when a large excess of dextrose (4 to 5 times the wt. of Bi salt) and of  $\text{NaOH}$  is taken. The reaction permits a quant. detn. of Bi, e. g., in subnitrate, but a simpler method, e. g., that of Vanino and Treubert (*Ber.* 1898, 1303) is preferable.

**Separation of copper from selenium.** A. ANGELETTI. *Gazz. chim. ital.* 53, 339-41 (1923).—Se cannot be detd. in solns. contg. Cu by means of  $\text{SO}_3$  owing to the pptn. of Cu with the Se (Brauner and Kurzma, *C. A.* 1, 2540). Other methods in use are tedious. A. found that Cu and Se may be sepd. quantitatively with cupferron. The method consists in pptg. the Cu as  $(\text{Ph}(\text{NO})\text{NO})_2\text{Cu}$  in the approved way with cupferron, in an acid soln., avoiding an unnecessary excess of cupferron, because in concg. the filtrate from the Cu detn. for the detn. of Se a red tar seps, probably composed of oxidation products of the reagent, which must be washed for a long time with  $\text{H}_2\text{O}$  and  $\text{HCl}$ . The filtrate is treated with concd.  $\text{HCl}$  and Se is pptd. with  $\text{SO}_3$ . Good results are given on the analysis of known mixts. of Cu and Se.

**A new volumetric method for the determination of nickel.** G. SPACU AND R. RAPAN. *Bul. soc. stiinte Cluj* 1, 325-31(1922); *Chem. Zentr.* 1923, II, 380.—The method is based on the complete pptn. of a sky-blue complex compd. of Ni from aq. soln. by K or  $\text{NH}_4$  thiocyanate in the presence of  $\text{C}_6\text{H}_5\text{N}$ , thus:  $\text{NiX}_2 + 4\text{C}_6\text{H}_5\text{N} + 2\text{NH}_4\text{CNS} \rightarrow [\text{Ni}(\text{C}_6\text{H}_5\text{N})_4](\text{CNS})_2 + 2\text{NH}_4\text{X}$ . An excess of 0.1  $N$   $\text{NH}_4\text{CNS}$  is added in the presence of  $\text{C}_6\text{H}_5\text{N}$  to the neutral or slightly acid Ni soln. and the  $\text{NH}_4\text{CNS}$  not reacting is titrated back with 0.1  $N$   $\text{AgNO}_3$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  being used as indicator. 2(CNS) corresponds to 1 Ni. Comparative expts. by electrolysis showed max. deviations of 0.11%.

**A new method for the detection of chlorine, bromine and iodine in the presence of thiocyanates.** G. SPACU. *Bul. soc. stiinte Cluj* 1, 332-4(1922); *Chem. Zentr.* 1923, II, 378.—By modifying slightly the previously described method for Cl and Br (*C. A.* 17, 1772), I also can be detected in the presence of thiocyanates. The method is based on the pptn. of the thiocyanate by a small excess of a soln. of a Ni salt and  $\text{C}_6\text{H}_5\text{N}$  without the simultaneous pptn. of chlorides, bromides or iodides (cf. preceding abstr.). The filtrate can then be tested for halogens by ordinary methods.

**A new gravimetric method for the determination of nickel and thiocyanates.** G. SPACU. *Bul. soc. stiinte Cluj* 1, 314-20(1922); *Chem. Zentr.* 1923, II, 380.—The method is based on the pptn. of Ni by  $\text{NH}_4\text{CNS}$  and vice versa (cf. preceding abstr.). An excess of concd.  $\text{NH}_4\text{CNS}$  and 10-20 drops of  $\text{C}_6\text{H}_5\text{N}$  (also representing an excess) are added at room temp. to the Ni soln. with stirring. After the amorphous blue ppt. is formed, the soln. is heated almost to boiling with stirring and again cooled gradually to room temp. The ppt. is decanted, washed free of  $\text{NH}_4\text{CNS}$  by 5% aq.  $\text{C}_6\text{H}_5\text{N}$ , dried in a porcelain crucible at  $130^\circ$ , incinerated slowly, and heated with a blast lamp for 2-3 hrs. To reduce traces of  $\text{Ni}_2\text{O}_3$  to  $\text{NiO}$ , the ultimate heating must be carried out with the crucible covered. The results obtained agree closely with those by electrolytic methods. By the converse procedure, thiocyanates can be detd., in which case one must not be misled by the blue sol. compd. which appears with the regular ppt. From the final wt. of  $\text{NiO}$ , the atm. of thiocyanate can be calcd. from the reaction:



**The assay of mono-sodium phosphate and phosphoric acid.** F. X. MOERK AND F. J. HUGHES. *Am. J. Pharm.* 95, 671-8(1923); cf. *C. A.* 17, 1200.—Expts. with phenolphthalein as indicator showed that  $\text{NaCl}$  was necessary for successful titrations, also

that carbonates in the standard alkali hydroxide soln. gave rise to discrepancies. Preliminary operations for phenolphthalein and Me red, resp., are described: To 100 cc. 10% NaCl soln. (free from Ca) add 0.2 cc. phenolphthalein indicator and standard NaOH soln. (free from carbonate) until a distinct red color is produced; divide the soln. into 2 equal portions, placing these portions in beakers of the same internal diameter. To one of these portions add 10 cc.  $\text{NaH}_2\text{PO}_4$  soln. (about 0.2 g.) and titrate with 0.1 N NaOH (free from carbonate) until the color matches that of the reserved portion. To 40 cc. of 0.1 N  $\text{AgNO}_3$  or an equiv. quantity of any other  $\text{AgNO}_3$  soln. add 0.2 cc. Me red and sufficient standard NaOH soln. just to change the red color to yellow, next add 10 cc.  $\text{NaH}_2\text{PO}_4$  soln. (about 0.2 g.) and titrate with 0.1 N NaOH (free from carbonate) until the supernatant liquid changes from pink to yellow (a drop of 0.1 N standard acid soln. should restore the pink color).

W. G. GARSSLER

**Determination of total sulfur in soils and silicate rocks.** W. M. SHAW AND W. H. MACINTYRE. *Ind. Eng. Chem.* 15, 1183-5 (1923).—The well known  $\text{Na}_2\text{O}_2$ - $\text{Na}_2\text{CO}_3$  fusion method has been found to give excellent results in the analysis of soils. Full details are given for carrying out the entire analysis.

W. T. H.

**The residue from silica-rock analysis.** M. AUROUSSAU. *J. Wash. Acad. Sci.* 13, 330-2 (1923).—In rock analysis the "main portion," about 1 g., is decompld. with 5 g. of  $\text{Na}_2\text{CO}_3$ , the cake treated with HCl and the  $\text{SiO}_2$  sepd. and driven off by HF. A residue is always left. The object of this study is to det. the nature and amt. of this residue. A sample of siliceous andesite was analyzed; it was found that 3 g. of the rock gave 0.0165 g. of this residue, which on analysis gave  $\text{Al}_2\text{O}_3$  0.07,  $\text{Fe}_2\text{O}_3$  0.14,  $\text{MgO}$  0.09,  $\text{CaO}$  0.01,  $\text{TiO}_2$  0.16,  $\text{P}_2\text{O}_5$  0.01,  $\text{SO}_3$  0.04, sum 0.52% calcd. to the original rock. This residue is not entirely lost in the usual procedure of analysis, since the  $\text{NH}_3$  ppt. of the filtrate from  $\text{SiO}_2$  is weighed with the residue in the same crucible. Ca, Mg and Ba are not recovered, but Ca and Ba are usually present in negligible amts. unless great accuracy is required. The  $\text{MgO}$  is 3.3% of that (2.77%) in the original rock.

J. W. RIGGS

**Analysis of silicates.** R. HARTA. *Rev. matériaux constructions trav. publics* 166, 156 (1923).—In analyzing silicates, decomposable by acids, especially cements, it has been found difficult to filter and sep. the  $\text{SiO}_2$ . Jaroslav Matejka has traced it to the influence of the chloride  $\text{SiCl}_4$ ,  $\text{CoCl}_2$ , in the presence of metatitanic acid. This may be remedied by the addn. of  $\text{NH}_4\text{Cl}$ .

LOUIS NAVIAS

**A new method for determining sulfur, arsenic and antimony in inorganic and organic compounds by "sinter-oxidation."** F. FEIGL AND R. SCHORR. *Z. anal. Chem.* 63, 10-29 (1923).—Mix 0.2-0.6 g. of the finely powdered substance with 2 g. of dry, powdered  $\text{KMnO}_4$  and 2 g. of  $\text{Na}_2\text{CO}_3$  in an 80-100-cc. Fe crucible. Cover the charge with 3 g. more of the fusion mixt. Heat the contents of the covered crucible 20-30 mins. over a small flame and for a somewhat longer period with the temp. gradually raised. In this way all S and As are converted into water-sol. Na sulfate and arsenate. Ext. the melt with water and add alc. if necessary to reduce Mn acids. Filter, wash with dil. NaOH and use the filtrate for the detn. of S and As. With Sb some difficulty is encountered and a part of this element remains undissolved by the water. By adding considerable alc. it can be made completely insol. and thus sepd. from As and S. Dissolve this residue in a mixt. of HCl and  $\text{H}_2\text{C}_2\text{O}_4$  and det. the Sb by one of the usual methods. If S and As are absent, the HCl and  $\text{H}_2\text{C}_2\text{O}_4$  can be added before filtering after the initial leaching of the melt. The method is easily carried out and the results obtained in the analysis of various inorg. and org. compds. indicate its accuracy.

W. T. H.

**The determination of fluorine in zinc blendes.** I. DA ROCHA-SCHMIDT AND K. KROCK. *Z. anal. Chem.* 63, 29-52 (1923).—The directions given in F. P. Treadwell's text for the detn. of F as  $\text{H}_2\text{SiF}_6$  by the method of S. L. Penfield are modified so that the S from sulfides does no harm and there is less danger of some  $\text{SO}_3$  being carried over with the  $\text{H}_2\text{SiF}_6$ . Mix 1 g. of the dry powder with 2 g. of pure, ignited quartz powder and 5 g. of anhydrous  $\text{CuSO}_4$ . Transfer this mixt. to the decompn. vessel and cover with 10 g. of  $\text{CrO}_3$ . Connect the decompn. vessel with a U-tube contg. dry glass beads and 2 Pélégot tubes each contg. 15 cc. of alc. satd. with KCl. Conduct dry  $\text{CO}_2$ -free air through the app. and decompose the fluoride with 20 cc. of anhydrous  $\text{H}_2\text{SO}_4$  which has been fumed to  $\frac{1}{2}$  of its original volume and cooled in an empty, dry desiccator. Otherwise the procedure is the same as described in the textbook.

W. T. H.

**The determination of nitrate in the presence of cyanamide and some of its derivatives.** K. D. JACOB. *Ind. Eng. Chem.* 15, 1175-7 (1923).—Cyanamide, dicyanodiamide and guanilurea can be removed from an aq. soln. by means of satd.  $\text{Ag}_2\text{SO}_4$  soln. and urea can be converted into  $\text{NH}_3$  by the action of urease and the  $\text{NH}_3$  distd.



off. After these interfering substances have been removed, the nitrate can be detd. by the Devarda alloy method. W. T. H.

**Stability of sodium thiosulfate solutions.** MARTIN KILPATRICK, JR., AND MARY L. KILPATRICK. *J. Am. Chem. Soc.* **45**, 2132-5(1923).—The stability of several 0.01 *N* solns. of  $\text{Na}_2\text{S}_2\text{O}_3$  has been studied over a period of 8 months. Freshly boiled redistd.  $\text{H}_2\text{O}$  gave a soln. that was more permanent than lab. distd.  $\text{H}_2\text{O}$ , ordinary redistd.  $\text{H}_2\text{O}$  or redistd.  $\text{H}_2\text{O}$  through which  $\text{CO}_2$ -free air had been bubbled.  $\text{CO}_2$ ,  $\text{O}$ , or dil.  $\text{NaOH}$  had very little effect on the stability of the soln. Decompn. is caused by the action of bacteria. E. P. WIGHTMAN

**Pyrotannic acid method for the quantitative determination of carbon monoxide in blood and air.** R. R. SAYERS, W. P. YANT AND G. W. JONES. *U. S. Public Health Repts.* **38**, 2311-20(1923).—See *C. A.* **17**, 2690. E. J. C.

**The Delbrouck method of measuring firedamp in pit air.** E. HUMBLET. *Colliery Guardian* **126**, 275(1923).—A simple method for detg.  $\text{CH}_4$  based on that of LeChatelier, is described. It consists essentially in substituting  $\text{H}_2\text{O}$  for  $\text{Hg}$  with the combustion app., a 1-l. flask of unoxidizable metal with a removable cover fitted with bow thumb-screw and gasket. The sample of gas is obtained by emptying the flask full of  $\text{H}_2\text{O}$  at the source and replacing the cover by another cover through which pass 2 elec. terminals connected by a Pt wire coated with Ir. A tube through the cover connects with a pressure gage. With the flask immersed in  $\text{H}_2\text{O}$ , the Pt is heated white for 10 min. with interruptions. From the decrease in pressure due to the reaction  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , the %  $\text{CH}_4$  can be calcd. by ordinary formulas. By a scale graduated in 1.03 mm. on each side of the 0 point, each degree corresponds to 0.01%  $\text{CH}_4$ . Fluctuations in atm. pressure are shown to be negligible, but the effect of temp. must be eliminated by cooling the flask to its original temp. before reading the gage. Comparative tests with the Orsat app. showed close concordance. The method is accurate to approx. 0.01%  $\text{CH}_4$ . C. C. DAVIS

**Detection of pentose, formaldehyde and methanol.** J. B. SUMNER. *J. Am. Chem. Soc.* **45**, 2378-80(1923).—A modification of the Bial orcinol reagent for pentoses is suggested which makes it suitable for the detection of  $\text{HCHO}$ . Aq. orcinol soln. can be used to advantage for detecting methanol in alcoholic liquids, which are first subjected to oxidation by  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ . C. A. R.

**Note on the estimation of the carbon content of solutions.** J. NEEDHAM. *Biochem. J.* **17**, 431-4(1923).—To det. the C content of solns. contg. 20 mg. or less of inositol and of bacterial culture mediums, an app. has been devised which effects the complete combustion of the org. compd., absorbs the  $\text{CO}_2$  in  $\text{Ba}(\text{OH})_2$  soln. and measures the vol. of  $\text{CO}_2$  in a Haldane gas buret after liberating it from  $\text{BaCO}_3$  by the action of tartaric acid. The liquid in a boat is introduced directly into an ordinary combustion tube and the combustion is carried out in the usual way but with special precautions for the removal of the unusually large quantity of  $\text{H}_2\text{O}$ . BENJAMIN HARROW

**Studies on inositol. I. A method of quantitative estimation.** JOSEPH NEEDHAM. *Biochem. J.* **17**, 422-30(1923).—The method consists in extg. the inositol with dil. acetone, pptg. with basic Pb acetate, decomp. the latter, and ultimately pptg. the inositol with abs. alc. or ether. The C in the inositol is detd. and from it the amt. of inositol calcd. BENJAMIN HARROW

**Analyses of chromium ores (CASTELLI) 8.** X-ray spectroscopy as a means of qualitative and quantitative chemical analysis (COSTER) 3. "Break" spark spectra and their use in chemical analysis (v. WELLSBACH) 3.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

**The properties of minerals and their interpretation in explaining the genesis of mineral species.** R. PAVANS DE CECCATY. *Rev. ind. minérale* **1923**, 155-76, 197-206, 220-32.—A review of the simple principles of geology, mineralogy and crystallography. C. C. DAVIS

**Change of pleochroism of kunzite by Becquerel rays.** KARL PRIZBRAM. *Ann. Akad. Wiss. Wien* **1922**, No. 22-3, 193-5.—The untreated kunzite is pleochroic in rose to colorless. When exposed to the rays, a California specimen gave corresponding colors of blue to yellow green, and one from Madagascar brown to yellow green. A. E. STERN

**Shattering of minerals and rocks about inclusions.** T. L. WALKER AND A. L.

PARSONS. *Univ. Toronto Studies, Geol. Ser. No. 16*, 25 (1923).—The following cases of shattering of rocks and minerals about inclusions are noted: quartz enclosing zircon and quartz enclosing ellsworthite from Hybla, Ont.; euxenite in orthoclase, Mabrey, Ont.; fluorite in quartz, Osterby, Sweden; allanite in granite, Seguin Falls, Ont. The shattering is ascribed to expansion of the inclusion in some cases, to contraction of the host in others. E. F. H.

**Crystals which have become isotropic.** O. MÖGGER. *Nach. Ges. Wiss. Göttingen (Math. phys. Klasse)* 1922, No. 2, 110-20. Among minerals which contain the rare earths in large amts. many are known which occur in isotropic crystals as evidenced by optical behavior and cohesion. In crystals from veins, parts are anisotropic and parts isotropic. When the latter are heated to redness they become birefringent and cannot be distinguished from original anisotropic ones. This change is accompanied by the liberation of heat. M. believes that these isotropic crystals were formed from normal anisotropic ones by bombardment with  $\alpha$ -particles through geologic periods, during which the crystals were under high pressure in the interior of the earth. Radioactive substances are always found in these crystals. The  $\alpha$ -particle bombardment produces random orientation of extremely small elementary crystals (almost of at. dimensions) so that the net effect is isotropic. Expts. on crystals of *gadolinite* are reported. M. also suggests that the rare earths, which are found in such surprisingly large amts. in radioactive minerals, may be decomposed products of more complex at. nuclei which have been subjected to  $\alpha$ -particle bombardment for long periods of time as in Rutherford's production of H from N. Evidence is advanced to favor this together with other interesting speculations on the rare earth minerals. S. K. ALLISON

**The crystallography of hydromagnesite.** A. P. ROGERS. *Am. J. Sci.* 6, 37-47 (1923).—By microscopic examn. of exceptionally well formed crystals of hydromagnesite,  $[Mg_3(OH)_2(CO_3)_2 \cdot 3H_2O]$  from Alameda Co., Cal., it is found that the mineral crystallizes in the monoclinic system. The crystals are invariably twinned on (100). The hardness = 3.5, sp. gr. = 2.152. The geometrical constns. are  $a:b:c = 1.1374:1.0:0.9034$ ,  $\beta = 65^\circ 52'$ ; and the optical:  $n_\alpha = 1.523 \pm 0.003$ ,  $n_\beta = 1.527 \pm 0.003$ ,  $n_\gamma = 1.545 \pm 0.001$ . S. K. ALLISON

**Some new occurrences of tellurides in Ontario.** E. THOMSON. *Univ. Toronto Studies, Geol. Ser. No. 16*, 38 (1923); cf. C. A. 17, 1937. Further occurrences of altaite, calaverite, sylvanite and tetradymite in Ontario are noted. E. F. H.

**Trevorite, a distinct mineral species.** T. L. WALKER. *Univ. Toronto Studies, Geol. Ser. No. 16*, 53-4 (1923).—The validity of trevorite (Crosse, C. A. 16, 2406) as a distinct species is confirmed by an analysis by Todd: Fe<sub>2</sub>O<sub>3</sub> 60.24, FeO 1.96, NiO 29.71, MgO 0.24, SiO<sub>2</sub> 1.40, H<sub>2</sub>O 0.36, sum 99.91%; sp. gr. 5.165. The state of oxidation was detd. by heating the mineral with H<sub>2</sub>SO<sub>4</sub> in a sealed tube in an atmosphere of CO<sub>2</sub>, and subsequent titration. The formula for trevorite is thus (Ni, Fe)O.Fe<sub>2</sub>O<sub>3</sub>. Examination showed it to be homogeneous. E. F. H.

**The mineral association of the salt deposits at Malagash, N. S.** H. C. RICKAHY. *Univ. Toronto Studies, Geol. Ser. No. 16*, 46-52 (1923). Six samples of salt gave 2-92% KCl. The sylvite is intergrown with halite, and is thought to have been deposited by circulating waters. Up to 0.1% Br was found in the samples. Anhydrite occurs with halite in thin layers. Associated small hexagonal crystals proved to be magnesite. They are mostly prismatic, and up to 5 mm. long. An analysis showed: MgCO<sub>3</sub> 89.29, FeCO<sub>3</sub> 0.58, CaSO<sub>4</sub> (as anhydrite inclusions in the crystals) 9.35%; sp. gr. 3.02. E. F. H.

**The identity of eakleite and xonotlite.** E. S. LARSEN. *Am. Mineral.* 8, 181-2 (1923).—Eakleite was described by L. (C. A. 11, 2082) as a new mineral, but published analyses of eakleite and xonotlite show them to be identical. This is confirmed by the optical and other physical properties. New data for xonotlite, from Tetela de Xonotla, Mexico:  $\alpha$  1.581,  $\gamma$  1.591, 2V small, optically +, elongation Z. The name xonotlite has priority. E. F. H.

**Notes on Canadian minerals—allanite, axinite, columbite, and sillimanite.** T. L. WALKER AND A. L. PARSONS. *Univ. Toronto Studies, Geol. Ser. No. 16*, 29-37 (1923).—Allanite is described from pegmatites at (1) Seguin Falls, Ont., and (2) Labelle Co., Que. They differ considerably in composition. Analyses (E. W. Todd):

	SiO <sub>2</sub>	ThO <sub>2</sub>	CaO	FeO	MnO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	etc.	Y <sub>2</sub> O <sub>3</sub>	etc.	H <sub>2</sub> O	Sum
1	31.88	0.44	12.94	9.56	0.74	1.03	16.66	4.91	19.58	1.64	1.33	100.71	
2	31.94	0.52	14.76	12.13	1.10	0.32	18.18	3.80	13.44	0.76	2.99	99.94	

Sp. gr. (1) 3.658, (2) 3.279;  $n$  (1) 1.735, (2) 1.650; (1) birefringence 0.01, (2) isotropic. Axinite from Marmora Twp., Hastings, Co., Ont. is found in a hornblende schist.

Analysis (Todd):  $\text{SiO}_2$  41.46,  $\text{B}_2\text{O}_3$  4.88,  $\text{Al}_2\text{O}_3$  19.94,  $\text{Fe}_2\text{O}_3$  0.96,  $\text{FeO}$  4.56,  $\text{MnO}$  5.44,  $\text{CaO}$  19.57,  $\text{MgO}$  1.99,  $\text{H}_2\text{O}$  1.61, sum 100.41, sp. gr. 3.221. The formula  $13\text{RO} \cdot \text{B}_2\text{O}_3 \cdot 10\text{SiO}_2$  is suggested for axinite. Columbite. Four analyses (Todd) are given: (1) crystals, Lavers Mine, New Ross, N. S.; (2) Hazaribagh, Bengal; (3) Lyndoch Twp., Renfrew Co., Ont.; (4) massive with visible rutile, Hybla, Ont. All are from pegmatites.

	$\text{Cb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{TiO}_2$	$\text{SiO}_2$	$\text{SnO}_2$	$\text{MnO}$	$\text{FeO}$	Sum	Sp. gr.
1	63.08	14.48	1.47	0.34	0.22	10.44	10.46	100.49	5.613
2	65.49	13.89	0.66	0.10	0.22	14.12	5.59	100.22 <sup>1</sup>	5.563
3	55.79	15.21	5.19	1.28	0.56	10.24	10.90	100.14 <sup>2</sup>	5.431
4	66.60	1.74	5.22	0.64	0.36	9.06	8.61	100.01 <sup>3</sup>	5.147

<sup>1</sup> Also 0.15  $\text{CaO}$ . <sup>2</sup> Also 0.15  $\text{CaO}$ , 0.82 rare earths. <sup>3</sup> Also 1.25  $\text{ZrO}_2$ , 3.44  $\text{ThO}_2$ , 1.68 rare earths, 1.41  $\text{H}_2\text{O}$ .

Sillimanite crystals, up to  $\frac{1}{2}$  inch long, occur in a gneiss at Romaine, Que. The mineral is colorless and transparent. Analysis (Todd):  $\text{SiO}_2$  36.70,  $\text{Al}_2\text{O}_3$  62.73,  $\text{Fe}_2\text{O}_3$  0.63, sum 100.06; sp. gr. 3.209.

E. F. H.

The North Mountain basalt of Nova Scotia: glaciation, tubular amygdaloid, mordenite and lousite. T. L. WALKER AND A. L. PARSONS. *Univ. Toronto Studies, Geol. Ser. No. 16*, 5-12(1923).—An analysis of a boulder clay is given. Tubular amygdaloid is widely distributed in the traps of N. S. The tubes, normal to the flow, are thought to be due to the escape of hot water vapors from the moist floor, through cracks in the chilled and solid underpart of the flow, into the still molten central portion. Three new localities for mordenite are noted in Kings Co., N. S. A reddish mordenite from Black Rock gave on analysis (E. W. Todd):  $\text{SiO}_2$  67.18,  $\text{Al}_2\text{O}_3$  12.36,  $\text{Fe}_2\text{O}_3$  0.24,  $\text{CaO}$  3.42,  $\text{Na}_2\text{O}$  3.34,  $\text{K}_2\text{O}$  0.47,  $\text{H}_2\text{O}$  13.23, sum 100.24%. Lousite, described as a new mineral by Honeymann in 1878, is shown to be a mixture of radiating quartz spherules and cleavable apophyllite. An analysis of the apophyllite, sepd. by heavy liquids, is given.

E. F. H.

Huronite from Gowganda, Ontario. T. L. WALKER. *Univ. Toronto Studies, Geol. Ser. No. 16*, 55-7(1923).—An analysis (by E. W. Todd) is given of porphyritic crystals from a diabase at Gowganda. They are composed of an exceedingly fine aggregate with  $n = 1.57$ -1.59, and birefringence only a little lower than that of augite. The analysis shows a close resemblance to some types of scapolite, a mineral frequently formed by the alteration of basic plagioclase.

E. F. H.

Ellsworthite and associated minerals from Hybla, Ont. T. L. WALKER AND A. L. PARSONS. *Univ. Toronto Studies, Geol. Ser. No. 16*, 13-20(1923).—Ellsworthite, named in honor of Dr. H. V. Ellsworth, is a new mineral found in pegmatite in Montecagle Twp., Hastings Co., Ont. It is massive, with no cleavage, adamantine luster, small conchoidal fracture,  $H = 4$ , isotropic,  $n > 1.74$ . There are 2 types: (1) amber yellow in color; (2) dark chocolate-brown. Sp. gr.: (1) 3.608, (2) 3.758. E. W. Todd found:

	$\text{Cb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{TiO}_2$	$\text{SnO}_2$	$\text{SiO}_2$	F	$\text{UO}_2$	$\text{UO}_3$
1	34.22	4.32	10.47	0.10	2.54	0.22	...	18.50
2	34.27	4.27	9.79	0.25	2.68	0.49	8.42	10.68

	$\text{CaO}$	$\text{MnO}$	$\text{PbO}$	Rare earths	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	Sum
1	11.73	0.43	0.24	0.21	4.10	0.42	12.23	99.72
2	13.62	0.22	0.41	...	3.80	...	11.42	100.32

The formula is  $\text{RO} \cdot \text{Cb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , with  $\text{RO} = \text{UO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CaO}$ ;  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{UO}_3$ , and  $\text{Ta}_2\text{O}_5$  replace  $\text{Cb}_2\text{O}_5$ . The types differ in oxidation of the U. Dehydration curves are given. The mineral is strongly radioactive: activity 1.02-1.11 as compared to that of pitchblende as 5.00. The U-Pb ratios indicate an age of 114 million yrs. for type 1, 197 for 2. Associated minerals are zircon, smoky quartz, microcline, oligoclase (crystals with 111, new for the mineral), pink calcite (color due to 0.21%  $\text{MnO}$ ), titanite, pyrrhotite, and chalcocopyrite.

E. F. H.

Hatchettolite and associated minerals from Hybla, Ont. T. L. WALKER AND A. L. PARSONS. *Univ. Toronto Studies, Geol. Ser. No. 16*, 21-4(1923).—The minerals described are from a feldspar quarry in pegmatite in Montecagle Twp., Hastings Co., Ont. Hatchettolite occurs in two types: (1) black, sp. gr. 4.509; (2) amber in thin splinters, sp. gr. 4.417. Both occur in irregular masses, and are isotropic with  $n > 1.74$ . E. W. Todd obtained by analysis:

	CbO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	UO <sub>2</sub>	SiO <sub>2</sub>	ZrO <sub>2</sub>	ThO <sub>2</sub>	SnO <sub>2</sub>	UO <sub>3</sub>
1	31.33	10.29	11.37	11.40	1.57	4.12	0.52	1.44	4.41
2	31.70	15.28	8.82	5.72	1.56	5.90	0.42	1.40	5.08
	CaO	Ce <sub>2</sub> O <sub>3</sub> etc.	Y <sub>2</sub> O <sub>3</sub> etc.	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O	PbO	MnO	H <sub>2</sub> O	Sum
1	13.25	0.12	0.62	3.46	0.30	0.54	0.51	4.29	99.60
2	13.62	0.50	0.62	3.63	0.20	0.24	0.43	5.05	100.23

The dark and light types are analogous to those of ellsworthite (preceding abstract). For both minerals the light types are probably secondary, derived from the darker type by hydration and oxidation. Dehydration curves are given. Hatchettolite has a radioactivity of 1.13 compared to that of pitchblende as 5.00. Zircon, variety cvrtolite, occurs with hatchettolite. Analysis (Todd): SiO<sub>2</sub> 26.14, Cb<sub>2</sub>O<sub>3</sub> 0.72, ZrO<sub>2</sub> 62.16, CaO 1.16, FeO 1.72, Fe<sub>2</sub>O<sub>3</sub> 2.06, UO<sub>2</sub> 1.26, H<sub>2</sub>O 4.21, sum 99.43% (sp. gr. 4.102). Cb and U are probably due to imperfectly separated hatchettolite. Columbite and garnet also occur here.

**Barrandite from Manhattan, Nevada.** E. V. SHANNON. *Am. Mineral.* 8, 182-4 (1923).—Barrandite has previously been described only from Příbram, Bohemia. The Nev. mineral is amorphous, opaque, olive-ocher in color, faint waxy in luster, and very brittle. The mean  $n$  is 1.640, birefringence 0.020; hardness 2. Analysis gave: SiO<sub>2</sub> 1.12, Al<sub>2</sub>O<sub>3</sub> 8.15, Fe<sub>2</sub>O<sub>3</sub> 30.00, P<sub>2</sub>O<sub>5</sub> 56.29, CaO 1.20, FeO 0.90, MgO 1.36, H<sub>2</sub>O 4-19.72, H<sub>2</sub>O—1.88%; formula (Fe, Al)<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.4H<sub>2</sub>O.

**The mineral resources of Russia. Iron ore at Krivoi-Rog.** ROPOR. *Rev. ind. minérale* 1923, 75-88.—Since the Fe ore is distinctly stratified and shows no crystals, geodes, sandbars or lodes, its formation is attributed to chem. pptn. followed by stratification. Decompn. of eruptive kersantite cong. hornblende and diorite occurring in dikes was caused by H<sub>2</sub>O and CO<sub>2</sub>. Specularite and hematite are the only forms of Fe which occur, and deposition took place at such temps. and pressures that CO<sub>2</sub> was liberated and no carbonated Fe formed. The surrounding earth contains chiefly SiO<sub>2</sub> and chlorite schists which, arising from the decompn. of the hornblende, were dissolved in the H<sub>2</sub>O of a lake while the clay and chlorite accumulated near the source of eruption. When the concn. became great enough, SiO<sub>2</sub> was deposited, and entrained particles of minerals with the formation of ferruginous quartzite. The present methods of exploitation are described and illustrated.

**Analyses of chromium ores.** G. CASTELLI. *Rass. min. met. chim.* 59, 1-4 (1923).—A general article dealing with the uses of Cr, its occurrence and the analysis of its ores. The detn. by 3 methods of Cr in ore is described, all of which methods involve its conversion (by fusion of the ore with KNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub>) to K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>: (1) pptn. of PbCrO<sub>4</sub>; (2) titration with FeSO<sub>4</sub> and (3) treatment of the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with HCl, treatment of the liberated Cl with KI and titration of the liberated I with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Widely scattered ores analyzed in % Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, CaO, MgO, SiO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>O, Cr and Fe, resp.: New Caledonia, 55.40, 13.19, 3.71, 12.77, 0.50, 11.90, 0.32, trace, 1.55, 37.89, 12.51; Rhodesia, 55.76, 10.06, 3.05, 14.45, 0.65, 13.32, 1.80, trace, 0.55, 38.14, 13.36; India (Baluchistan), 52.60, 11.32, 0.70, 13.30, 1.10, 16.40, 1.86, 0.10, 2.30, 35.98, 10.82; Greece (Volo), 51.10, 7.60, 1.03, 21.44, 0.60, 12.10, 4.50, 0.05, 1.30, 34.95, 17.38; Turkey (Macri), 44.45, 12.18, 14.22, —, —, 17.70, 6.20, 0.70, —, 30.40, 20.50.

**The Aztec Mine at Baldy, New Mexico.** C. A. CHASE AND D. MUIR. *Edel-Erd. und Erze* 4, 66 (1923).—The Aztec Mine, Baldy, Colfax Co., N. M., has been worked since 1868. In 1914 operations were begun in an altered slate carrying \$50-100 free Au/ton. Statistics of production, summary of previous papers on the geology, and methods of sepn. are given.

**The nature of the processes of ulmification and of coal formation.** H. J. PAGE. *Fuel* 2, 232-5 (1923).—A review and discussion.

**Vertical and lateral variations in the composition of bituminous coal seams.** H. BRIGGS. *Colliery Guardian* 125, 1507-8 (1923).—In regions where metamorphism by igneous intrusion is absent or slight, vertical and horizontal differences occur in the compn. of coal. This phenomenon is found in Durham and Northumberland, England, a detailed description of which is given with a map of "isovols."

**The tertiary brown coal forests of the Geiseltal.** R. ZANDER. *Braunkohle* 22, 17-25, 28-42 (1923).—A detailed study, by chem. and microscopic methods, of the origin of Geiseltal brown coal and the structure of the fossil vegetation from which it originated.

**Some brown coal and dysodite deposits of the Vogelberg.** K. HUMMEL. *Braunkohle* 22, 53-7, 68-74, 100-7 (1923).—A detailed description, with analyses, of the nature

and geologic characteristics of brown coal and dysodile in the Vogelberg. The brown coal is an indirect product of volcanic activity during the Miocene epoch and as a result the deposits show only slight horizontal extension and no great thickness, for the basin of volcanic origin is not of the same extent as the tectonic subsidence. The quality, however, has been improved by basaltic eruptions, as at Meissner. Dysodile is widely distributed (cf. Scheerer, *Braunkohle* 1912, 28). New distn. expts. of dysodile yielded in %:  $H_2O$  2-22, tar 0-6.48, coke 3.84-4.24, ash 75-95, gases 0.2-8.6. The Vogelberg dysodile is very similar in compn. to the slate coal of Messel. C. C. DAVIS

**Migration of petroleum in oil incrustations.** V. SACH. *Petroleum Z.* 19, 806-7 (1923).—Discussion of the theories of petroleum migration. Cf. *Ibid* 849-50. K. FRIEDL. Reply to Sach. D. F. BROWN

**Oil-yielding rocks in the Union of South Africa.** T. G. TREVOR. *Oil Eng. & Finance* 4, 253-6, 277-80, 301-5 (1923); *Petroleum World* 20, 358-60; *S. African J. Ind.* 6, 285-307.—The geological and geographical distribution of the oil-bearing rocks are described. The oil-yielding material of the Ermelo district is indistinguishable from the torbanite of Scotland and yields 22-98 gal. per ton of oil, while the other deposits resemble the usual shales or cannel coals. Each of the deposits is described in detail. D. F. BROWN

**The significance of Schreinemaker's work for the development of petrography.** J. H. L. VOGT. *Rec. trav. chim.* 42, 830-2 (1923).—An appreciation of S.'s contribution to the subject of phase rule studies as applied to petrography. E. J. WITZEMANN

**Analyses of rocks from the west edge of the dark granulitic massives.** D. MARCHET AND D. H. TERTSCH. *Anz. Akad. Wiss. Wien* 1921, No. 19, 171-3.—No. 1 is a granulitic rock, the principal one of the territory; 2, trap-granulite; 3, plagioclase-eclogite; and 4, a pyroxene-amphibolite.

	1	2	3	4
SiO <sub>2</sub>	70.09	67.49	47.35	47.39
TiO <sub>2</sub>	0.99	0.77	0.21	2.26
Al <sub>2</sub> O <sub>3</sub>	14.64	16.95	16.72	14.59
Fe <sub>2</sub> O <sub>3</sub>	0.93	0.13	0.34	2.45
FeO	2.23	4.77	6.91	9.38
MgO	1.00	0.59	12.42	7.26
CaO	2.04	2.60	14.09	12.17
Na <sub>2</sub> O	3.03	3.60	1.42	2.81
K <sub>2</sub> O	4.70	3.04	0.20	0.52
H <sub>2</sub> O <sup>+</sup>	0.40	0.35	0.22	0.63
P <sub>2</sub> O <sub>5</sub>	0.18	0.15	0.01	0.28
Sums	100.23	99.84	99.89	99.74

Loss of wt. at 110° varied from 0.14 to 0.57%.

A. E. STEARN

**The limestones of Ceylon.** J. S. COATES. *Tropical Agriculturist* 60, 156-8 (1923).—Analyses of 12 Ceylon limestones are given. Some are nearly pure calcite, but for the most part they are intergrowths of calcite and dolomite in varying proportions. Microscopic examn. shows an intimate intergrowth of the 2 minerals in alternating thin plates. M. S. ANDERSON

**Salt "seismograms," their tectonic and practical significance.** F. SCHÖNDORF. *Kali* 17, 193-7 (1923).—The salt beds found in certain German workings exhibit the undulating characteristics of seismographic records from which the term "salt seismogram" is derived. Their distinguishing characteristics are occurrence in almost all beds of the geologically young salt mountains, and local restriction to tectonically significant regions. Mineralogical and chem. investigations of salt "seismograms" are briefly reported. K. D. JACOB

**Migration of matter in metamorphism.** M. F. BECKE. *Anz. Akad. Wiss. Wien* 1922, No. 22-3, 195-7.—Contrary to Rosenbusch's idea that metamorphism is not accompanied by any essential change in chem. compn., a series of analyses shows a decrease in SiO<sub>2</sub> and feldspar bases (mostly K<sub>2</sub>O) and an increase in CO<sub>2</sub> and H<sub>2</sub>O, for samples of gneiss. Analyses were made of the outer layers of strongly exfoliated samples as well as of central portions. These were compared after calcg. the results on the basis of equal Al<sub>2</sub>O<sub>3</sub> content. A. E. STEARN

**The arid denudation and weathering forms of Saxon-Bohemian Switzerland as the result of organic weathering in the humid region.** F. KUNZ, F. PREISS AND E. BLANCK. *Biedermann's Zentr.* 52, 25-6 (1923).—Weathered sandstone shapes occurring in Saxon-Bohemian Switzerland are similar to those found in desert regions. The former are the result of the action of H<sub>2</sub>SO<sub>4</sub> and other acids produced by the decompn. of crude

humus, the erosive effect of running  $H_2O$ , and the peculiar chem. compn. of the sand-stones, while the latter are the result of the erosive action of wind and sand.

K. D. JACOB

The crystallization of certain salts in the magnetic field (ROASTO) 2. Residue from silica-rock analysis (ATROUSSEAU) 7. The systems  $KCl-MgCl_2-H_2O$  and  $NaCl-MgCl_2-H_2O$  (KRITIK) 6.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The American Iron and Steel Institute. H. H. COOK. *Army Ordnance* 4, 69-73, 76(1923).—Descriptive. E. J. C.

Cobalt. Its production and uses. C. W. DRURY. *Can. Chem. Met.* 7, 248-9 (1923). E. J. C.

The flotation process. E. BERL and H. VIERHILLER. *Z. angew. Chem.* 36, 161-4(1923).—By expts. on the effect of various dyes on the flotability of various minerals with benzene the following conclusions are arrived at. (1) The sp. gr. of finely divided solid phases is not of importance in the flotation process nor is the difference of sp. gr. of the liquids used. (2) Gases are not the cause of flotation. Their importance is in increasing the lifting force. (3) The nature of the surface of the solid body is of outstanding importance. (4) By covering a hydrophil colloid with a hydrophobe the hydrophil substance takes the properties of the hydrophobe. (5) The chemical and physical properties of the body are without appreciable influence on the flotability.

R. S. DEAN

Selective flotation of a complex zinc-lead ore. GEO. J. YOUNG. *Eng. Mining J. Press* 116, 453-6(1923).—The development of treatment of the Sullivan ore by the Consolidated M. & S. Co. of Canada is outlined and the process used in the new Kimberley mill described. Cf. C. A. 17, 2408. A. BUTTS

Leaching and extraction. Metallurgical leaching methods offer suggestions for chemical engineers. A. W. ALLEN. *Chem. Met. Eng.* 29, 671-5(1923).—The scope of the term leaching and some of the fundamentals of heap leaching have already been discussed (C. A. 17, 3390). The problems of vat leaching are discussed in the present article. The fineness of crushing and the proportioning of sizes should be governed by the factors (1) satisfactory extn., (2) rate of percolation, (3) short circuiting of soln., (4) no disarrangement of the fine and coarse particles, relative to one another. Condition (4) is essential to successful leaching. A. discusses the 4 conditions, using as illustrations the leaching of Cu ores in Ariz. and of caliche in Chile. The support for the charge must be properly designed and constructed, and A. gives considerable space to this. The term "filter bottom" should not be applied to the support, since it does not act as a filter. The leach should be clear at the time it leaves the charge, whether the leaching be downward or upward. If settling takes place, as it does in the upward leaching of caliche, it should take place evenly and regularly. Under such conditions of settling the method of drawing off the leach is important. Seven photographs.

E. C. R. ARDACH

Power plant problems of steel mills. L. B. BREEDLOVE. *Iron Age* 112, 1027-30 (1923). E. J. C.

Oxygen in steel making. F. W. DAVIS. *Iron Age* 112, 734-5(1923); cf. C. A. 17, 3471.—O might be used in the Bessemer process to lower the heat requirements for treating pig iron of P content too great for the acid process and too low for the basic process. Steel so produced would be of higher quality than ordinary Bessemer steel. O used in the open-hearth process would permit elimination of the regenerative system of obtaining high temp.; heat in the exhaust gases would be saved by waste-heat boilers. Better flame application could be had in such a non-reversing furnace, while construction and operation would be simpler and cheaper. High temp. could be obtained without complete combustion of the gas, giving a reducing atm. in the furnace when desired and enabling the making of steel of elec-furnace quality. Cheaper fuel could be used, and O might be used in place of ore as an oxidizing agent. Much time would thus be saved. Better refractories are needed to make some of these benefits possible.

A. BUTTS

Making tanning machine parts. PAR DWYER. *Foundry* 51, 811-6(1923). E. J. C.

**Magnesium in the foundry.** H. J. MAYBERRY. *Metal Ind.* **21**, 398-9(1923).—A description of methods of casting Mg and its alloys. E. J. C.

④ **Production of quality metals and alloys.** R. S. McBRIDE. *Chem. Met. Eng.* **29**, 745-51(1923).—A description of the processes used at the Huntington, W. Va. plant of the International Nickel Co., in the manuf. of monel metal and Ni. S. L. C.

**Structure changes in metals through cold working.** M. POLANYI. *Z. Physik* **17**, 42-53(1923).—The structure changes produced by drawing into wire and by rolling into foil are discussed. The fibrous structure produced in the former manner can be explained on the plausible assumption that slipping takes place most easily when the angle between the direction of the force and that of slip is greater than  $45^\circ$ . The foil structure can be explained on the following assumptions: (1) the rolling process is accompanied by a pressure effect normal to the plane of rolling, and a thrust in that plane, (2) a gliding plane manifests itself best when its angle with the rolling plane amounts to  $45^\circ$ , (3) a gliding direction is more effective the smaller the angle between it and the plane of thrust. More data may modify these views it is thought.

A. E. STERN

**Cohesion, hardness and toughness.** P. LUDWIK. *Z. Metallkunde* **14**, 101-10(1922); *J. Inst. Metals* **28**, 572. H. G.

**New studies on recrystallization.** W. FRAENKEL. *Z. Metallkunde* **13**, 148-51(1921).—A review of papers appearing elsewhere. S. L. CHISHOLM

**Photomicrography as applied to the iron-carbon alloys.** J. W. BAMFYLDE. *Phot. J.* **63**, 360-70(1923).—The use of photomicrographs in the iron-steel industry is outlined. Photomicrographs of the various forms of steel are given showing the structure as produced by heat treatment with varying percentages of C. The segregation of S in steel is easily shown by squeegeeing a piece of bromide paper soaked in 5%  $H_2SO_4$  on the surface of the steel. After sufficient darkening by the  $H_2S$  the print is washed, fixed and dried. C. E. K. MEES

**Brittleness of tin containing aluminium.** E. HEYN and E. WETZEL. *Z. Metallkunde* **14**, 335-6(1922).—Cases of extreme brittleness in supposedly pure Sn were traced to the presence of 0.22-0.26% Al. Such an alloy after being cast becomes brittle very rapidly if placed in a salt soln. and extremely slowly if kept in a desiccator. If after chemical action is complete the material is remelted, an Al-free Sn is obtained, the Al as oxide remaining as a powder. The presence of Pb up to 10% does not affect this behavior. The presence of Cu below 2% greatly delays this chem. action, and above 2% almost completely inhibits it. Alloys of Sn with 5-98% Al were unchanged over long periods in air, but decomposed with gas evolution in salt solns. and more slowly in distd. water. Alloys with 98-99.5% Al were not stable in electrolytes. S. L. CHISHOLM

**Bearing metals for railroad use.** J. KARAFIAT. *Montan. Rundschau* **15**, 392-4(1923).—A series of Sn-Cu-Sb-Pb alloys has been investigated in steps of 5% Sn replacing Pb. The properties tested include Brinell hardness, impact, and compression strengths. For 10% Sn the optimum Cu content was 8%; for 20% Sn the optimum Sb was 16%, for 20-50% Sn, 14% Sb, and over 50% Sn, 13% Sb. Alloys with less than 15% Sn have little elasticity. For the requirements of locomotives and coaches various trade alloys were also tested. For such bearings alloys with 75% or more Sn give the best results. "Turbo-squirrel" alone, of the trade alloys tested, gave equal results. The lab. tests were closely checked by actual results in operation. S. L. CHISHOLM

**The question of the replacement of copper by other metals.** E. K. SCHULZ. *Z. Metallkunde* **14**, 321-8(1922); *J. Inst. Metals* **28**, 771.—This report deals with the substitution of other metals for Cu in the manuf. of driving bands for shells during the war scarcity in Germany. The combination of qualities met with in Cu is found in no other metal, and some have to be sacrificed. With Cu the thermal and mech. treatment proved to be more important than the exact degree of purity. Tensile, Brinell, bending and shearing tests were required. Brass was tried as a substitute, but the Cu had to be over 63% to give sufficient softness when rolled, and although extruded brass with higher zinc gave greater saving, trouble was caused by volatilization and burning of zinc. Three alloys of zinc were used with success, contg. Cu, 2, or Al-4, or Cu 1.3 and Al 2.3%. These alloys were prepd. by melting the zinc first and adding either molten Al or granulated rich alloys, followed by extrusion, the final section being given by rolling or drawing. Annealing after pressing and rolling must be avoided. Soft iron was also used with success. Electrolytic iron was not easily obtained in sufficiently thick sheets and had to be annealed, but a satisfactory method was found in bundling the thin strips, and welding as in making puddled scrap. Low-C open-hearth steel was also used,

the elastic limit being lowered by annealing the cold-worked metal so as to cause grain growth and globularize the cementite. H. G.

**Determinations of the density of metals and alloys at high temperatures. III. The system tin-bismuth.** K. BORNEMANN AND PAUL SIEBE. *Z. Metallkunde* 14, 329-34 (1922); cf. *C. A.* 16, 3844.—The sp. vols. of Sn, Bi, and Sn-Bi alloys have been detd. at temps. up to 900°. In every case, the vol. is directly proportional to the temp. Sn expands 2.8% during melting, and Bi contracts 3%. J. C. S.

**Cold rolling and annealing of some copper zinc alloys.** PENDLEPOWELL. *Brass World* 19, 218, 335 (1923).—A translation of the German thesis by Fried. Koerber and P. J. H. Wieland. See Wieland (*C. A.* 17, 1415). C. G. F.

**The knowledge of the aluminium-zinc alloys.** W. SANDER AND K. L. MEISSNER. *Z. Metallkunde* 14, 385-7 (1922); *J. Inst. Metals* 29, 633.—The alloys at the Al end of the series have been studied, with special reference to the change of solid soly. with temp. Al and zinc of 99.7% and 99.5% purity, resp., were used. The specimens were quenched after being maintained at a given temp. for from 16 to 48 hours, and etched for 10 to 15 minutes in HNO<sub>3</sub> (d. = 1.28). The results obtained differ considerably from those of Hanson and Cayler. While the latter authors find that the dystectic at 256° only extends to 65% of Al, the new results extend the limit to 83%, and show a steeper slope of unmixing the curve, which meets the concn. axis at 92% instead of 83. The sepn. of a second solid phase is also indicated by a change of elec. cond. H. G.

Comparison of the dilatation curve and the thermic curve (LOSANA) 2. Metallurgical requirements of refractories for use in the Al industry (ANDERSON) 19. Solid solutions (ROSENHAIN) 2. Electrical conductivity and constitution of alloys. (II) system Bi-Tl (GUERTLER, Schulze) 2.

VAN PATTEN, NATHAN: **Bibliography of the Corrosion of Metals and its Prevention.** 2025 entries with notes. 180 pp. The author, Queen's Univ. Library, Kingston, Ontario, Can. \$5.00.

**Treating pyritic copper ore.** W. E. GREENAWALT. U. S. 1,468,806, Sept. 25. Pyritic Cu ore or concentrate is roasted until most of the S is eliminated and most of the Fe present is converted into oxide. Small quantities of pyritic ore are then added to the hot partly roasted material and Cu is leached out after completion of the roasting.

**Apparatus for amalgamating ores.** C. MEYER AND H. B. MEADE. U. S. 1,469,007, Sept. 25.

**Flotation separation of zinc sulfide ores.** G. A. HILLSTRAND. U. S. 1,469,042, Sept. 25. An ore contg. ZnS together with other metal sulfides such as those of Pb and Fe is treated with a sol. sulfide such as Na sulfide in an amt. not exceeding 7 lbs. per ton of ore, to inhibit the flotation of ZnS and the treated ore is then subjected to flotation sepn. of other constituents without flotation of more than a small part of the ZnS.

**Separating copper from zinc.** C. BERTHELOT. U. S. 1,468,988, Sept. 25. A soln. contg. both Cu and Zn, e. g., a soln. from ores or alloys, is treated with H<sub>2</sub>S, the pptd. Cu sulfide is removed from the soln. and the latter is then utilized for dissolving additional metal.

**Wrought iron.** J. ASTON. U. S. 1,469,373, Oct. 2. The molten metal from a steel-making operation is poured into molten slag and granulated in it while maintaining the temp. of the molten slag below the m. p. of the metal during the operation. U. S. 1,469,374 specifies adding Si (as ferro-Si) or other non-carbonaceous protective metalloids to a molten steel product and then mixing it in granulated form with a slag of puddling properties, to obtain wrought Fe. Cf. *C. A.* 16, 2104.

**Coating iron or steel with zinc spelter.** J. L. HERMAN. U. S. 1,468,905, Sept. 25. Wire or other articles of Fe or steel are provided with a flexible and malleable coating by first coating with Zn spelter and then, without wiping the coating, heating to about 675° for a short time.

**Removing rust or scale from iron or steel.** H. N. HOLMES. U. S. 1,470,225, Oct. 9. Fe or steel is pickled in a bath of H<sub>2</sub>SO<sub>4</sub> contg. at least 0.2% of an aldehyde, e. g., CH<sub>3</sub>O, BzH, furfural or AcH, to inhibit the attack of the acid on the metal.

**Alloying molten metals.** C. VOS. U. S. 1,469,706, Oct. 2. Alloys such as ingredients of special steels are formed into a cylindrical body with a central opening through it and this body is introduced beneath the surface of molten metal, e. g., steel, in a furnace and allowed to dissolve while supported by a holder which is afterward withdrawn from the furnace.



**Copper aluminium alloy.** O. NAJACHT. U. S. 1,468,828, Sept. 25. An alloy which resembles bronze is formed of Cu 3 lbs., Al 1.5 oz. and constituents of ordinary brass 8 oz.

**Alloy steel.** P. A. E. ARMSTRONG. U. S. 1,468,937, Sept. 25. An alloy steel which is adapted for manuf. of impact tools is formed mainly of Fe together with C 0.3-0.6, Mn 0.2-0.6, Si 0.2-0.6, Cr 0.75-1.75, W 1.0-2.5 and V 0.1-0.85%.

**Tungsten ingot.** J. A. YUNCK. U. S. 1,469,761, Oct. 2. An ingot of W or W alloy is formed by packing fine powder mainly composed of W into a cylinder of Cu or other soft ductile metal, closing the ends of the cylinder with plugs of the same metal, swaging down the cartridge thus formed to about  $\frac{1}{3}$  its original diam. and then heating in a C tube in an non-oxidizing atm. to volatilize the Cu or other enveloping metal and firm the W together.

**Roller feed furnace for annealing metal sheets or other metal articles.** H. L. I. SCHRECK. U. S. 1,468,837, Sept. 25.

**Gold solder.** W. SHEFF and H. M. SHEFF. U. S. 1,469,191, Sept. 25. Au 66 Ni 7, Zn 16 and Cu 15 parts.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER AND CLARENCE J. WEST

**The possibility of using chlorosulfonic acid for the absorption of ethylene from gaseous mixtures.** W. TRAUBE and R. JUSTH. *Brennstoff-Chem.* 4, 150-4(1923).  $C_2H_4$  may be quickly and quant. absorbed from coke-oven gases by  $ClSO_3H$  with the formation of the Et ester. The use of Br is not advisable as an absorption agent owing to its high cost and limited use of the product. Fuming  $H_2SO_4$  absorbs  $C_2H_4$  quant., but it is not possible to obtain EtOH from this combination by any known method. Concd.  $H_2SO_4$  absorbs  $C_2H_4$  although not quant. The absorption reagent experimented with consists of a mixt. of 1 part 100%  $H_2SO_4$  and 1 part  $ClSO_3H$ . The gas contg. the  $C_2H_4$  must be free from moisture. As some  $ClSO_3H$  or  $ClSO_3Et$  is carried into the gas stream it is necessary to have a soda-lime tube connected with the app. to absorb these vapors. The  $ClSO_3H$  takes up about 82% of the theory of  $C_2H_4$ . The  $ClSO_3Et$  b.  $\approx 155-60^\circ$  undecomd.  $H_2O$  reacts with it as follows:  $ClSO_3Et + 2H_2O = EtOH + HCl + H_2SO_4$  and  $ClSO_3Et + H_2O = ClEt + H_2SO_4$ . 84% of the ester reacts according to the 1st equation and the remaining 16% according to the latter.

C. T. WHITE

**Addition of water to ethylene and propylene.** J. P. WIBAUT and J. J. DIEKMANN. *Proc. Acad. Sci. Amsterdam* 26, 321-8(1923).—When a mixt. of  $H_2O$  vapor and  $C_2H_4$  is passed over  $Al_2O_3$  or  $Al_2(SO_4)_3$  at  $300-400^\circ$ , the reaction product contains some AcH (0.2-0.4%). That this is not due to oxidation of the  $C_2H_4$  was shown by passing a mixt. of air and  $C_2H_4$  over  $Al_2O_3$  at  $360^\circ$ ; the 1st step must be the addn. of  $H_2O$  to the double bond, forming EtOH.  $C_2H_4$  behaved similarly, 0.2-0.3% AcMe being formed. In studying the action of an acid catalyst, an app. was devised in which an ascending stream of gas came into intimate contact with the descending acid. By using 65%  $H_2SO_4$  at  $156-160^\circ$ , and passing  $C_2H_4$  at the rate of 1 l. per hr., about 5% conversion into EtOH took place. Practically no reaction took place with 55% acid. 90-96%  $H_2SO_4$  absorbs  $C_2H_4$  readily; 85% absorbs it after 20 min. and 80% after 1 hr.'s shaking. The reaction with 96% acid at  $0^\circ$  gave little  $C_2H_5HSO_4$ . The hydration of  $C_2H_4$  by hot dil.  $H_2SO_4$  is possible, with the above app., but the reaction velocity is low, which renders the yield small. Further, the  $H_2SO_4$  decomp. a large part of the  $C_2H_4$ . At lower temp. and with a more concd. acid, condensation products are formed.  $PhSO_3H$  and  $C_6H_5$  gave 1.5% alc.

C. J. WEST

**The constituents of wood spirit oil.** H. PRINGSHEIM and J. LEIBOWITZ. *Ber.* 56B, 2034-41(1923).—A sepn. of the components by fractional distn. at atm. and reduced pressures was not found satisfactory because of the great no. of distns. necessary and also because of the decompn. of some of the compds.  $NaHSO_3$  treatment was used partially to sepn. the mixt. into 3 portions: (a) cryst. addn. compds. of aldehydes and ketones, (b) soln. of the oil in  $NaHSO_3$  soln., yielding mesityl oxide and similar unsatd. ketones, (c) the portion not affected by  $NaHSO_3$  consisting of hydrocarbons, alcs., etc. Group (a) addn. compds. were decompd. with  $H_2SO_4$  and the compds. sepd. by fractional distn. and then identified by conversion into cryst. derivs.; aldehydes were also identified by reaction with ammoniacal  $Ag_2O$  and oxidation to the acids. The following compds. were isolated and identified: trimethylacetaldehyde,  $Me_3CCHO$ , b.  $74^\circ$ ;  $MeCOEt$ , b.  $80-1^\circ$ ;  $iso-BuCHO$ , b.  $92^\circ$ ;  $iso-PrCOMe$ , b.  $92^\circ$ ;  $MeCOPr$ , b.  $102^\circ$ ; methyl- $\alpha$ -butenyl

**ketone (2-keto-3-hexene) (I),**  $\text{MeCOCH} \cdot \text{CHEt}$ , b. 122–4°; **cyclopentanone (II),** b. 129–30°. *Dumasin* (cf. Fittig, *Ann.* 110, 17 (1859); Pinner, *Ber.* 15, 586 (1882)), which occurs in the fraction 120–30°, was found to be a mixt. of I and II. The original wood spirit oil was also extd. with NaOH soln. and only one acid was found; viz., a *dihydroxyacetic acid*,  $\text{C}_2\text{H}_4(\text{OH})_2\text{CO}_2\text{H}$ , the structure of which was not detd. I, which has never been isolated previously, is very readily decompd. on distn. and was identified by oxidation to  $\text{AcCO}_2\text{H}$ ; *pyruvic acid p-nitrophenylhydrazone*, m. 118°, is useful as an indicator for acidimetry, being very sol. in alkalis, giving in dilns. of 1:2000 an intense red color which changes sharply to light yellow on acidification.

N. A. LANGR

**Manufacture of methyl and ethyl ethers.** J. H. SENDERENS. *Compt. rend.* 177, 15–9 (1923); cf. *C. A.* 17, 1949.—MeOH added at 130° to acids of various strengths gave the following vols. per min. of  $\text{Me}_2\text{O}$ :  $\text{H}_2\text{SO}_4$  24.0 cc;  $3\text{H}_2\text{O}$  120 cc;  $4\text{H}_2\text{O}$  24 cc. It is quite possible to make  $\text{Me}_2\text{O}$  almost continuously by supplying MeOH to  $\text{H}_2\text{SO}_4$  at 160–5°, at which temp. the ratio  $\text{H}_2\text{SO}_4$ : $2\text{H}_2\text{O}$  is maintained. This method works excellently for any quantities; "but of course for large scale production the catalytic dehydration of MeOH would be used."

BEN. H. NICOLLET

**Decomposition of ether-oxides by metallic sodium.** J. F. DURAND. *Bull. soc. chim.* 33, 734–5 (1923). Schorigin, who published in the same field (*C. A.* 17, 1208), overlooked priority (*C. A.* 15, 1282) of D., who wishes to reserve the field. B. H. N.

**Yields of some Grignard reagents.** HENRY GILMAN AND ROY MCCrackEN. *J. Am. Chem. Soc.* 45, 2462–6 (1923); cf. *C. A.* 17, 530. Following the technic which had been found to give the best yield of  $\text{EtMgI}$  (1.25 g. Mg turnings, the amt. of org. halide calcd. for 1.15 g. Mg and a small crystal of I, the halide in  $\text{Et}_2\text{O}$  being added in the course of 45 min. and the mixt. being stirred constantly), various halides were found to give the following % yields of the Grignard reagent (detd. as described in the earlier paper):  $\text{PrI}$  79.35,  $\text{BuI}$  65.23,  $\text{AmI}$  75.76, hexyl iodide 59.50, heptyl iodide 64.27, octyl iodide 44.22, lauryl bromide 73.70,  $\text{BuBr}$  91.24, *iso*  $\text{BuBr}$  78.23, *sec*  $\text{BuBr}$  68.26, *tert*  $\text{BuBr}$  20.62,  $\text{BuCl}$  87.38,  $\text{PhBr}$  94.37,  $\text{PhI}$  84.58, *o*  $\text{MeC}_6\text{H}_4\text{Br}$  86.65, *m*  $\text{MeC}_6\text{H}_4\text{Br}$  84.75, *p*  $\text{MeC}_6\text{H}_4\text{Br}$  88.16,  $\text{PhCH}_2\text{Cl}$  94.28, *n*  $\text{C}_6\text{H}_{13}\text{Br}$  70.50, bromocyclohexane 68.32, *o*-bromostyrene 47.59.

C. A. R.

**Catalytic decomposition of amides.** A. MAHLE. *Mit. grasses* 15, 6488–91, 6531–3 (1923); *Caoutchouc & gutta-percha* 29, 11829–32, 11898–900.—M. showed in 1906 that hydrogenation of primary amides on Ni at 230° gives a mixt. of primary and secondary amines:  $\text{RCONH}_2 + 2\text{H}_2 \rightarrow \text{RCH}_2\text{NH}_2 + \text{H}_2\text{O}$  and  $2\text{RCH}_2\text{NH}_2 = (\text{RCH}_2)_2\text{NH} + \text{NH}_3$ . Hydrogenation in the presence of Cu at 200° gives the same results. Bochner and Andrews dehydrated primary amides by heating at 250–60° in the presence of pumice,  $\text{Al}_2\text{O}_3$ , sand or lampblack, with formation of the corresponding nitriles:  $\text{RCONH}_2 = \text{H}_2\text{O} + \text{RCN}$ . In prepg. nitriles by action of  $\text{NH}_3$  on esters in the presence of  $\text{Al}_2\text{O}_3$ , when the reaction temp. is 120–10°, a considerable proportion of primary amides is formed:  $\text{RCO}_2\text{Et} + \text{NH}_3 = \text{EtOH} + \text{RCONH}_2$ .  $\text{NH}_3$  also gives primary amides with satd. fatty acids in the presence of  $\text{Al}_2\text{O}_3$  at 430–50°:  $\text{RCO}_2\text{H} + \text{NH}_3 = \text{H}_2\text{O} + \text{RCONH}_2$ . *Arylformamides* are easily prepd. by heating phenolic amines for a short time with  $\text{HCO}_2\text{H}$ , and distil practically unchanged at atm. pressure. *Formanilide*, m. 46°, b. 284°, in the presence of  $\text{Al}_2\text{O}_3$  at 400° gives off CO and traces of H and  $\text{CO}_2$ , with formation of a large amt. of  $\text{PhNH}_2$  and a little  $\text{PhCN}$ . The reactions involved are  $\text{PhNHCHO} = \text{CO} + \text{PhNH}_2$ ,  $\text{PhNHCHO} = \text{H}_2\text{O} + \text{PhNC}$ ,  $\text{PhNC} = \text{PhCN}$ ,  $\text{PhNC} + \text{H}_2\text{O} = \text{PhNH}_2 + \text{CO}$ ,  $\text{PhNHCHO} + \text{H}_2\text{O} = \text{PhNH}_2 + \text{HCO}_2\text{H}$ ,  $\text{HCO}_2\text{H} = \text{CO}_2 + \text{H}_2$ , the first predominating. Similar results are obtained in the presence of finely divided Ni at 330–40°. When catalyzed by Ni at 400–10°, the gas evolved consists of  $\text{CO}_2$  26, CO 48,  $\text{H}_2$  26%, and sym-diphenylurea, m. 235°, is formed:  $\text{PhNHCHO} + \text{PhNH}_2 = \text{CO:NHPh}_2 + \text{H}_2$ . This occurs only in the presence of a considerable excess of  $\text{HCONHPh}$ , and not when it is led over the catalyzer in small quantities. *o*-Formotoluidide, m. 63°, b. 289°, obtained by heating mol. equivs. of *o*-toluidine and  $\text{HCO}_2\text{H}$  for 20 min., in the presence of  $\text{Al}_2\text{O}_3$  at 400° gives off CO and *o*-toluidine, but no tolunitrile could be identified. In the presence of Ni at 400° it gives gas (CO 34, CO 41,  $\text{H}_2$  25%), *o*-toluidine, and sym-di-*o*-tolylurea, m. 241°. *m*-Formotoluidide, b. 288°, in the presence of  $\text{Al}_2\text{O}_3$  at 400° gives CO, *m*-toluidine, and a small amt. of *m*-tolunitrile. On Ni at 400° it gives gas (CO 10, CO 50,  $\text{H}_2$  40%), *m*-toluidine, and sym-di-*m*-tolylurea, m. 203°. *p*-Formotoluidide, m. 57°, when slowly passed over Ni at 350° gives a small amt. of CO with traces of  $\text{CO}_2$  and  $\text{H}_2$ , and *p*-toluidine. When passed rapidly over Ni at 400–10° it gives a large amt. of gas (CO 44, CO 16,  $\text{H}_2$  40%), *p*-toluidine and sym-di-*p*-tolylurea, m. 243°. *o*-Formoxylidide, m. 97°, prepd. by boiling  $\text{HCO}_2\text{H}$  with *o*-xylidine, in the presence of Ni at 400° gives gas (CO 17, CO 66,  $\text{H}_2$  17%), *o*-xylidine, and sym-di-*o*-xylylurea, m. 236°. The low  $\text{CO}_2$  content of the gas is pre-

sumably due to the fact that the Ni was not very active. *Formo*[methyllethylanilide], 2,4-MeEtC<sub>6</sub>H<sub>3</sub>NHCHO, m. 151°, prep'd. by boiling equimol. amts. of HCO<sub>2</sub>H and of MeEtC<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> in the presence of Ni at 400–20°, gives gas (CO<sub>2</sub> 27, CO 35, C<sub>2</sub>H<sub>4</sub> 2, CH<sub>4</sub> 9, H 27%), MeEtC<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>, b. 230°, and *sym-di-2-methyl-4-ethylphenylurea*, obtained in this manner for the first time. *Methylanilineformamide* (*N*-methylformanilide), PhNHMeCHO, prep'd. by boiling equimol. amts. of PhNHMe and HCO<sub>2</sub>H for 20 min., b. 288°, in the presence of Ni at 400–10° gives gas (CO<sub>2</sub> 26, CO 47, H 27%, PhNHMe, and *sym-dimethyl-diphenylurea*, CO(NMePh)<sub>2</sub>, b. 245–6°. *m*-Methyllethylformanilide (*N*-ethylform-2-methyl-4-ethylanilide), 2,4-MeEtC<sub>6</sub>H<sub>3</sub>NHCHO, m. 141°, in the presence of Ni at 400° gives gas (CO<sub>2</sub> 22, CO 53, H 25%), MeEtC<sub>6</sub>H<sub>3</sub>NHCHO, b. 230°, and *sym-diethyl-di-methyllethylphenylurea*, b. 295°. *Ethyl-o-toluidineformamide* (*N*-ethylform-*o*-toluidide), b. 272°, in the presence of Ni at 400° gives gas (CO<sub>2</sub> 14, CO 52, H 32, C<sub>2</sub>H<sub>4</sub> 2%), C<sub>6</sub>H<sub>4</sub>MeNH<sub>2</sub>Et, and *sym-diethyl-di-o-tolylurea*, b. 258–60°. *N*-Isoamylformamide, b. 237°, in the presence of Al<sub>2</sub>O<sub>3</sub> at 420° gives CO, iso-AmNH<sub>2</sub>, iso-AmCN (C<sub>6</sub>H<sub>11</sub>NHCHO = H<sub>2</sub>O + C<sub>6</sub>H<sub>11</sub>NC, C<sub>6</sub>H<sub>11</sub>NC = C<sub>6</sub>H<sub>11</sub>CN), and iso-AmNH<sub>2</sub> carbonate; in the presence of Ni at 360° it gives gas (CO<sub>2</sub> 12, CO 18, H 18, C<sub>2</sub>H<sub>4</sub> 5, CH<sub>4</sub> 47%), and a liquid consisting almost entirely of iso-AmCN, which partly breaks up into NH<sub>3</sub> and isomylene, the latter in turn slightly breaking down to lower hydrocarbons, particularly CH<sub>4</sub>. Hydrogenation of iso-AmNHCHO in the presence of Ni at 200–10° gives a mixt. of C<sub>6</sub>H<sub>11</sub>NHMe, b. 108°, and of C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>, with traces of NH<sub>3</sub> and of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. Anilides of AcOH and of its higher homologs, in presence of Ni, give off CO with formation of the corresponding secondary amine, which breaks down to PhNH<sub>2</sub>. *Acetanilide*, passed slowly over Ni at 400° gives gas (CO<sub>2</sub> 14, CO 36, CH<sub>4</sub> 3, H 47%, with traces of NH<sub>3</sub>), a little C<sub>2</sub>H<sub>4</sub>, a large amt. of PhNH<sub>2</sub>, some (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and a little unchanged AcNHPh. With fresh and very active Ni, the decomn. products are C, NH<sub>3</sub> and fixed gases (CO<sub>2</sub> 5, CO 20, CH<sub>4</sub> 25, H 45%). Pptd. Cu at 410°, and Al<sub>2</sub>O<sub>3</sub> give practically the same results as ordinary divided Ni. *o*-Acetotoluidide on Ni at 420° gives *o*-toluidine and gas (CO<sub>2</sub> 9, CO 42, CH<sub>4</sub> 12, H 37%). *m*-Acetotoluidide on Cu at 410° gives *m*-toluidine and gas (CO<sub>2</sub> 21, CO 9, H 60%). *o*-Propiotoluidide on Ni gives *o*-toluidine and gas contg. 5% of C<sub>2</sub>H<sub>4</sub> hydrocarbons. *Acetamide* on Ni at 400° gives gas (CO<sub>2</sub> 24, CO 14, CH<sub>4</sub> 20, H 42%), NH<sub>3</sub> and MeCN. *Butyramide* gives PrCN, b. 116°, NH<sub>3</sub>, H<sub>2</sub>O, and gas (CO<sub>2</sub> 19.5, CO 10, CH<sub>4</sub> 27.7, H 42.8%). *iso*-Valeramide on Ni at 370° gives valeronitrile, b. 129°, a little isovaleric acid, and gas (CO<sub>2</sub> 18, CO 11, C<sub>2</sub>H<sub>4</sub> 6, CH<sub>4</sub> 30, H 35%).

A. PAPINEAU-COUTURE

The synthesis of the methyl ester of  $\beta$ -methylaminopropene- $\alpha$ -carboxylic acid. T. V. KORSCHUN AND K. V. ROLL. *Bull. soc. chim.* 33, 1106–7 (1923).—Me  $\beta$ -methylaminopropene- $\alpha$ -carboxylate, prep'd. from MeNH<sub>2</sub> and AcCH<sub>2</sub>CO<sub>2</sub>Me, m. 60.5°. It can be titrated with H<sub>2</sub>SO<sub>4</sub> with rosolic acid as indicator.

A. C. PURDY

The isonitriles. V. Reaction with levulinic acid. MARIO PASSERINI. *Gazz. chim. ital.* 53, 331–3 (1923).—As was previously stated (C. A. 17, 1632) org. acids acting upon aromatic nitriles generally give diarylformamidine salts while the same comp'd. with ketones and aldehydes gives arylamides of acylated  $\alpha$ -HO acids. Levulinic acid (I) may react with PhNC in 1 of 2 forms: MeCOCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H or Me(HO)C(O.CO.CH<sub>2</sub>CH<sub>2</sub>). The results show that it reacts in the latter form, giving  $\beta$ -an-

ilido- $\beta$ -hydroxybutane- $\beta$ , $\delta$ -dicarboxylic acid lactone, (II), PhNHCOCMe.O.CO.CH<sub>2</sub>CH<sub>2</sub>.

5 g. PhNC dild. with 1 vol. of Et<sub>2</sub>O were treated with 7 g. I; after 10 days the Et<sub>2</sub>O was allowed to evaporate and after 4 weeks the odor of PhNC was nearly gone. The residue was dissolved in the minimum of hot 60% EtOH. This was repeated with the oil sep'd. on cooling, whereupon II sep'd. as an amorphous product, m. 44–6°. When 1 g. was sapon'd. by boiling 4 hrs. in 10 cc. H<sub>2</sub>O + 10 cc. conc'd. HCl, PhNH<sub>2</sub> was obtained on extg. the product with Et<sub>2</sub>O and  $\beta$ -hydroxybutane- $\beta$ , $\delta$ -dicarboxylic acid, m. 68–70°, from the aq. soln.

E. J. WITZEMANN

Salts of maleic, fumaric and inactive malic acids. J. M. WEISS AND C. R. DOWNS. *J. Am. Chem. Soc.* 45, 2341–9 (1923).—The data in the literature regarding the salts of the 3 acids are reviewed. The H<sub>2</sub>O of crystn. of a no. of these salts has been det'd., the results in some cases not agreeing with those of previous workers. The following salts are new: *Ca acid fumarate*, CaC<sub>4</sub>H<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O; *Co maleate* (11H<sub>2</sub>O); *Co i-maleate* (3H<sub>2</sub>O); *Ni i-maleate*; *Mn<sup>+</sup> acid maleate* (4.5H<sub>2</sub>O); *Mn<sup>++</sup> maleate* (3H<sub>2</sub>O); *Cu i-maleate* (2H<sub>2</sub>O); *Cd fumarate* (anhyd.) and *maleate* (2H<sub>2</sub>O); *Na antimonyl i-maleate*; *Ag fumarate*. Below are given the H<sub>2</sub>O of crystn., if any, and the soly. in 100 parts H<sub>2</sub>O at 30° (unless otherwise stated) of a no. of these salts: Fumarates: Cd, 0.09; Ca acid, 2H<sub>2</sub>O, 5.19; Ca, 3H<sub>2</sub>O, 1.66; Co, 4H<sub>2</sub>O, 0.88; Cu, 2H<sub>2</sub>O, 0.02; Pb, 0.025; Mn<sup>++</sup>, 0.14; Ni, 5H<sub>2</sub>O.

0.36; Ag, 0.013; Na acid, 6.87 (25°), 10.74 (40°), 18.15 (60°), 30.2 (100°); Na, 22.83 (25°); Sr, 0.29; Zn, 5H<sub>2</sub>O, 1.96. Maleates: Cd, 2H<sub>2</sub>O, 0.66; Ca acid, 5H<sub>2</sub>O, 21.13 (25°), 41.89 (40°), 94.78 (60°); Ca, 1H<sub>2</sub>O, 2.49 (25°), 2.88 (40°); Cu, 1H<sub>2</sub>O, 0.12; Pb 0.052; Ag, 0.12; Na acid, 3H<sub>2</sub>O, 6.73 (25°), 12.81 (40°), 31.3 (60°), 288.0 (100°); Na, 0.5H<sub>2</sub>O, 96.06 (25°). Pb *l*-malate, 0.5H<sub>2</sub>O, 0.21. C. A. R.

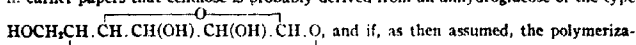
**Dihydroxymaleic (dihydroxyfumaric) acid.** J. BOESEKEN AND J. G. DE VOOGE. *Rec. trav. chim.* 42, 745-9 (1923).—Fenton (*J. Chem. Soc.* 65, 809 (1894)) obtained dihydroxymaleic acid (I) by oxidizing tartaric acid with H<sub>2</sub>O<sub>2</sub> in the presence of some FeSO<sub>4</sub>. He believed that I with HBr in glacial AcOH gives the isomer dihydroxyfumaric acid (II). Skinner (*J. Chem. Soc.* 73, 482 (1898)) found that I and II have the same dissociation const., whereas B. and de V. say that that of II should be much lower than that of I. The identity of I and II has again been proved by detg. their conduct with respect to H<sub>2</sub>BO<sub>3</sub>. The increase in elec. cond. of H<sub>2</sub>BO<sub>3</sub> produced by 0.5 *M* solns. of both preps. (I and II) was the same, which would not be the case if they were really *cis-trans* isomers (*Ibid.* 37, 170 (1917); cf. C. A. 12, 2515). Both preps. show the same decompn. into CO<sub>2</sub> and HIOCH<sub>2</sub>CHO. H<sub>2</sub>BO<sub>3</sub> exercises a similar protective action on this decompn. in both preps. The position of the OH and CO<sub>2</sub>H in I has not been definitely detd. E. J. WITZMANN

**New syntheses from hydrocyanic acid by means of the electric discharge.** I. FRANCESCOINI AND ADOLFO CIVRLO. *Gazz. chim. Ital.* 53, 327-30 (1923).—F. and C. are repeating the work of Berthelot on this subject in order to see how C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub> behave under exptl. conditions practically realizable: i. e., at ordinary temp. under the action of light and of the elec. discharge and a high temp. with and without catalysts. The interpretation of the genesis and constitution of the compds. formed will be emphasized. When a mixt. of C<sub>2</sub>H<sub>2</sub> + N<sub>2</sub> was subjected to the elec. discharge, a strong odor resembling that of isonitriles was observed. In similar expts. with C<sub>2</sub>H<sub>4</sub> + N<sub>2</sub> the same result was obtained: C<sub>2</sub>H<sub>4</sub> + N<sub>2</sub> → 2HCN + H<sub>2</sub>; C<sub>2</sub>H<sub>4</sub> + HCN → EtCN. In other expts. HCN was passed with C<sub>2</sub>H<sub>2</sub> through a Berthelot electrizer or ozonizer and gave EtNC and EtCN. These preliminary results are briefly discussed and further results are promised. E. J. WITZMANN

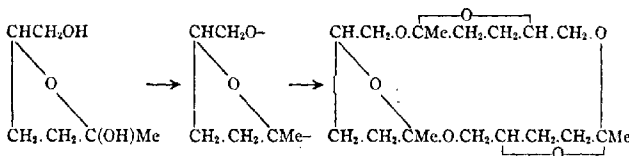
**Oxidation of glucose by the yellow oxide of mercury, and the preparation of gluconic acid.** LEONCE BERT. *Bull. soc. chim.* 33, 733-4 (1923).—As others have disagreed, B. once more recommends the oxidation of glucose by boiling with a water suspension of freshly precipitated HgO. One gets very readily 60% of pure cryst. *mercurous gluconate*, as shown by analysis. BEN H. NICOLET

**Fluoroacetyl derivatives of sugars. II. Optical rotation and atomic dimension.** D. H. BRAUNS. *J. Am. Chem. Soc.* 45, 2381-90 (1923); cf. C. A. 17, 2107. —Comparison of the specific optical rotations of the monohaloacetyl derivs. of glucose, cellose, xylose and fructose shows that the differences F-Cl, Cl-Br and Br-I are approx. proportional to the differences in at. diam. of these elements given by Bragg. The relations between at. diam. and various other properties (chem. affinity or reaction velocity, b. p., mol. vol., at. refraction) are briefly discussed. *Fluorotetraacetylfructose*, obtained in 5 g. yield from 10 g. of β-pentaacetylfructose (I) like the glucose compd., m. 112°, [α]<sub>D</sub><sup>20</sup> —90.43° (1.4803 g. made up to 25 cc. in CHCl<sub>3</sub>), mol. wt. in C<sub>6</sub>H<sub>6</sub> 338-50. *Bromotetraacetylfructose* (4 g. from 10 g. I and HBr in AcOH), m. 65°, [α]<sub>D</sub><sup>20</sup> —189.1° (0.8188 g. in 25 cc. CHCl<sub>3</sub>), is very unstable, decomp. perceptibly in 25 min. at room temp., can be kept overnight at —10° in pure H<sub>2</sub>O or CHCl<sub>3</sub>. C. A. R.

**Cellulose chemistry. IV. Properties of γ,δ-dihydroxycarbonyl derivatives and their bearing on the polymerization of polysaccharides.** HAROLD HIBBERT AND J. A. TROM. *J. Am. Chem. Soc.* 45, 2433-9 (1923); cf. C. A. 17, 1434. —It was suggested in earlier papers that cellulose is probably derived from an anhydroglucose of the type



tion of the latter to cellulose is fundamentally related to the behavior of the γ- and aldehydic HO groups and dependent on the loss of H<sub>2</sub>O from them, other γ,δ-dihydroxycarbonyl derivs. should presumably exhibit the same behavior. Such has been found to be the case. HOCH<sub>2</sub>CH(OH)CH<sub>2</sub>CH<sub>2</sub>COMe (I) when heated at 120-30° in the presence of a trace of mineral acid (H<sub>2</sub>SO<sub>4</sub>) for a few min. evolves 1 mol. H<sub>2</sub>O per mol. I and forms a dark very viscous product solidifying at room temp. to a hard compact resin. Assuming that I has the butylene oxide structure, the change taking place may presumably be represented as follows:



That there is not a primary elimination of  $\text{H}_2\text{O}$  from I to form  $\text{O.CH}_2\text{CHCH}_2\text{CH}_2\text{COMe}$

(II) was shown by directly synthesizing II; this shows no tendency to polymerize when heated with a drop of concd.  $\text{H}_2\text{SO}_4$ , prolonged heating resulting only in charring. I,  $b_{7-8}$  158–60°,  $b_{8-9}$  189–91°, was obtained in 8 g. yield from 12 g. Na, 70 g.  $\text{AcCH}_2\text{CO}_2\text{Et}$  and 50 g. epichlorohydrin by Traube and Lehmann's method (*Ber.* 34, 1971(1901)); it is a pale yellow viscous liquid which dists. *in vacuo* without decompn. if all traces of acid are carefully removed and apparently undergoes no change for months at room temp. The II,  $b_{81}$  169°, was obtained in about 2 g. yield from 10 g. allylacetone by Kablukov's method (*J. Russ. Phys. Chem. Soc.* 1, 502(1887)).

**Action of chloral on cellulose.** J. H. ROSS AND J. M. PAYNE. *J. Am. Chem. Soc.* 45, 2363–6(1923).—Cotton cellulose (50 g.) allowed to stand 12 hrs. with 100 g.  $\text{CCl}_3\text{CHO}$ ,  $\text{H}_2\text{O}$  in 100 cc. concd.  $\text{H}_2\text{SO}_4$  gave no chloral-substituted cellulose or cellulose dextrins. Four compds. were isolated from the reaction mixt. I, m. 268°, insol. in hot or cold alkalis, is *l*-rotatory in  $\text{C}_6\text{H}_5\text{N}$ , does not reduce Fehling soln., gives with  $\text{Ac}_2\text{O}$ - $\text{H}_2\text{SO}_4$  a monoacetate, m. 198°,  $[\alpha]_D -12^\circ$  ( $\text{CHCl}_3$ , c 5 (g. in 100 cc. soln.)); *Me ether*, prepd. with alk.  $\text{Me}_2\text{SO}_4$ , m. about 200°,  $[\alpha]_D -17^\circ$  (1:1  $\text{Me}_2\text{CO}$ - $\text{C}_6\text{H}_5\text{N}$ , c 5). II, m. 225°,  $[\alpha]_D -15^\circ$  ( $\text{CHCl}_3$ , c 1.2), insol. in alkalis, does not reduce Fehling soln.; acetate, m. 126°,  $[\alpha]_D -21.4^\circ$  ( $\text{CHCl}_3$ , c 4.67); *Me ether*, m. about 110°,  $[\alpha]_D -23^\circ$  ( $\text{CHCl}_3$ , c 5). III, m. 136–6°,  $[\alpha]_D 32^\circ$  ( $\text{C}_6\text{H}_6$ , c 7.754), 10.5° ( $\text{CHCl}_3$ , c 7.617), sol. in cold concd.  $\text{HNO}_3$ , insol. in alkalis, does not reduce Fehling soln. even after boiling with acids. IV, very impure, m. about 74–5°,  $[\alpha]_D 11^\circ$  ( $\text{CHCl}_3$ , c 8.12), insol. in alkalis, reduces Fehling soln. after boiling with acids. I and II correspond in every way to the 2 known dichloralglucoses; III and IV have approx. the same compn. as I and II. The same 4 compds. are similarly formed from starch and glucose. Parachloralose is formed when the crude  $\text{H}_2\text{O}$ -insol. products of starch and glucose, but not those of cellulose, are boiled. The sol. reaction products from all 3, however, give parachloralose when dild. and heated on the  $\text{H}_2\text{O}$  bath.

**Cymylmagnesium chloride.** LEONCE BERT. *Compt. rend.* 177, 195–7(1923).—Cumyl chloride and Mg in  $\text{Et}_2\text{O}$  form some dicumyl, but the chief product is the Grignard compd., whose reactions, apparently normal, are being followed further.

**Phenol derivatives of cymene.** G. BARGELLINI. *Gazz. chim. ital.* 53, 234–45 (1923).—The poly-HO derivs. of cymene are known only in part. Of the 4 di-HO derivs. only 2 are known. Neither of the 2 tri-OH cymene derivs. was previously known, but both are described here. When thymoquinone (I) was treated with  $\text{Ac}_2\text{O}$  (+ a little concd.  $\text{H}_2\text{SO}_4$ ) (Cf. Thiele, *Ber.* 31, 1247(1898)) the tri-AcO derivs., 4,2,3,6- and 4,2,3,5-Me(AcO) $_3\text{C}_6\text{H}_3\text{CH}_3$  (II and III), of cymene were obtained. The prepn. of I from thymol by way of nitrosothymol and aminothymol is described. I was reduced with  $\text{SO}_2$  to thymohydroquinol (IV), m. 139°; with  $\text{AcCl}$  it gives the *di-Ac deriv.*, m. 73–5°. 20 g. I were added slowly to 60 g.  $\text{Ac}_2\text{O}$  + 2 cc. concd.  $\text{H}_2\text{SO}_4$  at 40–50°. After 12–24 hrs. the mixt. was poured into  $\text{H}_2\text{O}$ . The oily layer consisting of II and III crystd. slowly and the isomers were sepd. by crystn. from  $\text{EtOH}$ . The less sol. 2,3,5-triacetoxycymene (II), m. 135–7°. The other 2,5,6-isomer, (III), m. 83–5°. II is sapond. in concd.  $\text{H}_2\text{SO}_4$  in 24 hrs. This soln. when poured into  $\text{H}_2\text{O}$  and extd. with  $\text{Et}_2\text{O}$  gave a reddish oil. The trihydroxycymene was not isolated out oxidized with  $\text{H}_2\text{SO}_4$  +  $\text{FeCl}_3$  to 3-hydroxythymoquinone, (V), m. 181–3°. V with  $\text{Ac}_2\text{O}$  + Zn dust gave II. III treated similarly gave 6-hydroxythymoquinone (VI), m. 166–8° and this with  $\text{Ac}_2\text{O}$  + Zn dust gave III. Attempts to prep. dihydroxythymoquinone (VII) from VI by oxidation with  $\text{H}_2\text{O}_2$  and with  $\text{K}_2\text{S}_2\text{O}_8$  failed. VII was more easily obtained from V and VI by dissolving them in  $\text{KOH}$  or  $\text{NaOH}$  and passing air through the solns. On acidifying the soln. VII sepd. in red laminas from  $\text{EtOH}$ , m. 222–4°. VII in  $\text{EtOH}$  reduced with  $\text{H}_2$  + Pt black gave tetrahydroxycymene (Henderson and Boyd, *C. A.* 4, 3214) but it could not be isolated. 5 g. VII + 50 g.  $\text{Ac}_2\text{O}$  + 15 g. Zn dust were heated on a sand bath and then poured into  $\text{H}_2\text{O}$ : tetraacetoxycymene (VIII), m.

186–8°, sepd. If V or VI is heated with  $\text{Ac}_2\text{O}$  and the hot soln. treated with  $\text{H}_2\text{SO}_4$  VIII is formed. V or VI treated with  $\text{Ac}_2\text{O} + \text{H}_2\text{SO}_4$  at room temp. is recovered unchanged.

**Reaction of carbon disulfide on *p*-phenylenediamine.** C. E. BOLSER AND E. H. HARTSHORN. *J. Am. Chem. Soc.* **45**, 2349–55 (1923).—It is stated in a patent (Win. Noetzel & Co., *Ber.* **24**, 849 (1891)) that  $\text{CS}_2$  and  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  (I) in alc. give  $(p\text{-H}_2\text{NC}_6\text{H}_4\text{NH})_2\text{CS}$  (II) and a product (III), insol. in cold dil. acids and all ordinary solvents, designated as *p*-phenylenethiourea,  $\text{C}_6\text{H}_4\text{NH}_2\text{CSNH}_2$ . In carrying out this reaction

it was found that when the usual procedure of prolonged boiling in alc. was followed only a very small amt. of the reaction product consisted of II. To avoid the formation of III one of the  $\text{NH}_2$  groups in I was protected by acetylation, but while  $p\text{-H}_2\text{NC}_6\text{H}_4\text{NHAc}$  readily gave with  $\text{CS}_2$  the expected  $(\text{AcNH}\text{C}_6\text{H}_4\text{NH})_2\text{CS}$  all attempts to hydrolyze this to II resulted in decompn. and formation of I. By carrying out the reaction between I and  $\text{CS}_2$  at a lower temp. with a reduced concn. of  $\text{CS}_2$  and frequently removing by filtration the II formed, which is relatively only slightly sol. in alc. at the lower temp., it was found that the yield of II could be increased; when  $\text{H}_2\text{O}$ , in which II is much less sol., is used instead of alc. in a specially devised app. in which the temp. can be kept near the b. p. of  $\text{CS}_2$  and the concn. of the latter can be maintained low, the formation of III can be almost entirely suppressed. This indicates that III is not a primary product of the reaction but is formed secondarily from II, and as a matter of fact II with  $\text{CS}_2$  in alc. forms an insol. compd. (IV) in approx. the amt. demanded by the equation  $\text{II} + \text{CS}_2 = \text{SC}(\text{NH}\text{C}_6\text{H}_4\text{NH})_2\text{CS} + \text{H}_2\text{S}$ . Neither III nor IV is obtained pure, apparently because of the occlusion of impurities from which the products, on account of their insol., cannot be freed by crystn., but both decomp. above 285°, give I with hot concd. acids and are decompd., although extremely slowly, by boiling  $\text{Ac}_2\text{O}$  with formation of  $p\text{-C}_6\text{H}_4(\text{NCS})_2$  (V). There is no doubt, therefore, that III and IV are the same substance, *p*-diphenylenedithiourea. With boiling  $\text{AcOH}$  II gives III, which is also obtained in small amts. when it is attempted to hydrolyze  $p\text{-AcNH}\text{C}_6\text{H}_4\text{NCS}$  (VI); apparently the free  $\text{H}_2\text{NC}_6\text{H}_4\text{NCS}$  is incapable of existence, in soln. at least, but at once forms III, a view confirmed by the fact that when  $p\text{-PhN:N}\text{C}_6\text{H}_4\text{NCS}$  (VII) is reduced in  $\text{AcOH}$  with  $\text{SnCl}_2\cdot\text{HCl}$ , the mustard oil does not under these conditions (lower temp. and presence of  $\text{HCl}$ ) at once form the thiourea, as in boiling  $\text{AcOH}$ , but does form it as soon as the clear acid soln. is made sufficiently alk. to dissolve the  $\text{Sn}$  hydroxides and set free the base. *o*-Diacylaminothiophenylthiourea (10.2 g. from 10 g.  $p\text{-H}_2\text{NC}_6\text{H}_4\text{NHAc}$  in alc. refluxed 10 hrs. with an excess of  $\text{CS}_2$ , m. 235–7°; 10 g. boiled with  $\text{Ac}_2\text{O}$  gives 4.1 g. *p*-acetylaminothiophenyl isothiocyanate (VI), m. 195–6°. *Azobenzene-p*-isothiocyanate (VII) (8.4 g. from 15 g.  $p\text{-PhN:N}\text{C}_6\text{H}_4\text{NH}_2$  boiled with  $\text{CS}_2\text{Cl}_2$  in  $\text{CCl}_4$ , salmon-colored, m. 94–5°).

***p*-Nitrobenzeneazopyrogallol (chrome brown P. A.).** P. JULLIARD. *Bull. soc. chim.* **33**, 1084–9 (1923).—*p*-Nitroaniline was diazotized and added to cold aq. pyrogallol and  $\text{NaOAc}$ . The *p*-nitrobenzeneazopyrogallol sepd. out and was filtered off. It is insol. in water, sol. in alc., and dissolves in  $\text{NaOH}$  with a reddish blue color. On fractional crystn. of its alc. soln. 2 isomers were obtained. The first crystals dissolved in  $\text{NaOH}$  with a blue-violet color and gave a triacetate, m. 193°. The same triacetate was obtained from the crude product. The mother liquor deposited a smaller amt. of a product, dissolving with a red-violet color in alkali. Because of the fastness of the dye, the more abundant isomer is probably the one having the  $\text{OH}$  ortho to the chromophore, *N:N*. *Chrome brown A. N.*, prepd. from  $\text{PhN:NPh}$  and pyrogallol dyes a more yellow-brown than chrome brown P. A.

**Influence of sulfur on the color of azo dyes.** W. R. WALDRON AND E. E. REID. *J. Am. Chem. Soc.* **45**, 2399–417 (1923).—Two classes of dyes have been considered: (1) Those derived from monoamines, particularly those from  $p\text{-MeSC}_6\text{H}_4\text{NH}_2$  and  $p\text{-MeSO}_2\text{C}_6\text{H}_4\text{NH}_2$ , and also some contg. other radicals than  $\text{Me}$  attached to the S; the influence of the S, however, overshadows that of the radical. The  $\text{MeS}$  group has been found to be an even stronger chromophore than  $\text{MeO}$  but oxidation to  $\text{MeSO}_2$  destroys this effect entirely, this group being actually hypsochromic. (2) Dyes derived from diamines which may be regarded as benzidine with various groups between the 2 rings. Apparently, the peculiar properties of benzidine dyes are lost when the 2 rings are sepd.; on the contrary, a base like  $(\text{H}_3\text{NC}_6\text{H}_4\text{SCH}_2)_2$  resembles  $\text{H}_2\text{NC}_6\text{H}_4\text{SMe}$ . The S and  $\text{SO}_2$  groups have the same effects in the di- as in the monoamino dyes. In all the dyes made S has a decided bathochromic effect if joined directly to the ring carrying the azo chromophore group but has little effect when sepd. from the ring by even a  $\text{CH}_2$  group. The general method of prep.

the amines consisted in condensing a halide with  $p\text{-O}_2\text{NC}_6\text{H}_4\text{SNa}$  or  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$  with the Na salt of a mercaptan and reducing 1 portion of the product to the  $\text{NH}_2$  sulfide and oxidizing another portion to the sulfone and then reducing it to the  $\text{NH}_2$  sulfone. *p*-Nitrothiophenol ethers (% yields in parentheses): Me, m.  $72^\circ$ , yellow (71); Et, m.  $44^\circ$ , yellow (76); *iso*-Pr, m.  $44.5^\circ$ , yellow (76); Pr, brown oil,  $d_{25}^{25}$  1.1963 (71); *iso*-Bu, brown oil,  $d_{25}^{25}$  1.1573 (78); Bu, brown oil,  $d_{25}^{25}$  1.1625 (71); *iso*-Am, brown oil,  $d_{25}^{25}$  1.1335 (70); PhCH<sub>3</sub>, yellow, m.  $123^\circ$  (73); phenacyl, yellow, m.  $118^\circ$  (98); hydroxyethyl, yellow, m.  $59^\circ$  (82); bromoethyl, yellow, m.  $58^\circ$  (86). Esters, obtained with  $\text{BzCl}$ ,  $\text{COCl}_2$  and  $\text{CsCl}$ , resp.: Benzoate, yellow, m.  $123.7^\circ$  (54) ( $\text{NH}_2$  ester, m.  $115^\circ$  (75)); carbonate, yellow, m.  $174.5^\circ$  (64); thiocarbonate, buff, m.  $141^\circ$  (55). *p*-Aminothiophenol ethers (all but 2 are oils rapidly darkening in the light), prepd. from the  $\text{NO}_2$  ethers with Fe dust and a trace of AcOH: Me,  $d_{25}^{25}$  1.1425 (97); Et,  $d_{25}^{25}$  1.1010 (95); *iso*-Pr (82); Pr (88); *iso*-Bu,  $d_{25}^{25}$  1.0421 (93); Bu (93); *iso*-Am (92); Ph, m.  $95.8^\circ$  (62); PhCH<sub>3</sub>,  $d_{25}^{25}$  1.1321 (81); phenacyl, m.  $111.5^\circ$  (87). *p*-Nitrophenyl alkyl sulfones, prepd. from the sulfides with  $\text{CrO}_3\text{-AcOH}$ : Me, m.  $142.5^\circ$  (84); Et, m.  $138.5^\circ$  (76); *iso*-Pr, m.  $115.3^\circ$  (86); Pr, m.  $114^\circ$  (86); *iso*-Bu, m.  $73^\circ$  (87); Bu, m.  $56.4^\circ$  (70); *iso*-Am, m.  $62.5^\circ$  (70); Ph, m.  $142^\circ$  (88); PhCH<sub>3</sub>, m.  $172^\circ$  (97).  $\text{NH}_2$  sulfones: Me, m.  $133^\circ$  (70); Et, m.  $89.3^\circ$  (46); *iso*-Pr, m.  $122^\circ$  (80); Pr, m.  $97^\circ$  (92); *iso*-Bu, m.  $83.7^\circ$  (91); Bu, m.  $109^\circ$  (91); *iso*-Am, m.  $110^\circ$  (92); Ph, m.  $176^\circ$  (90); PhCH<sub>3</sub>, m.  $218.5^\circ$  (89). *p*-Nitrobenzyl alkyl sulfides, from  $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$  and Na mercaptides: Bu, oil,  $d_{25}^{25}$  1.1482 (76.6); *iso*-Am, oil,  $d_{25}^{25}$  1.1513 (94); Ph, m.  $79^\circ$  (74.3).  $\text{NH}_2$  sulfides: Bu,  $d_{25}^{25}$  1.0321 (89); *iso*-Am,  $d_{25}^{25}$  1.0307 (41); Ph, m.  $72^\circ$  (94). *p*-Nitrobenzyl alkyl sulfones: Bu,  $d_{25}^{25}$  1.1395 (50); *iso*-Am,  $d_{25}^{25}$  1.177 (75); Ph, m.  $209.5^\circ$  (88).  $\text{NH}_2$  sulfones: Bu, m.  $95^\circ$  (85); *iso*-Am, m.  $126^\circ$  (71); Ph, m.  $180^\circ$  (62). *p*,*p'*-Dinitrophenyl derivatives,  $(\text{O}_2\text{NC}_6\text{H}_4)_2\text{X}$ , where X is 1 of the following groups: —S—, m.  $154^\circ$ , orange (36); —CH<sub>2</sub>S—, m.  $108^\circ$ , pale yellow (94); —(CH<sub>2</sub>)<sub>2</sub>S—, m.  $159^\circ$ , yellow (95); —SCH<sub>2</sub>S—, m.  $179^\circ$ , olive (83); —S(CH<sub>2</sub>)<sub>2</sub>S—, m.  $136^\circ$ , yellow (60); —S(CH<sub>2</sub>)<sub>3</sub>S—, m.  $110^\circ$ , yellow (91); —SCHPhS—, m.  $150.5^\circ$ , yellow (75); —(SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S—, m.  $86.5^\circ$ , yellow (76); —(SCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SO<sub>2</sub>—, m.  $170^\circ$ , pale yellow (77). *Di-NH<sub>2</sub> compds.*: —S—, m.  $108^\circ$ ; —CH<sub>2</sub>S—, m.  $93^\circ$  (76); —(CH<sub>2</sub>)<sub>2</sub>S—, m.  $105^\circ$  (38); —SCH<sub>2</sub>S—, m.  $99^\circ$ , red (92); —S(CH<sub>2</sub>)<sub>2</sub>S—, m.  $111^\circ$ , red (88); —S(CH<sub>2</sub>)<sub>3</sub>S—, oil (87); —SCHPhS—, m.  $131^\circ$  (88); —(SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S—, m.  $93^\circ$ , red (88); —(SCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SO<sub>2</sub>—, m.  $149^\circ$  (97). *Di-NO<sub>2</sub> sulfones*: —SO<sub>2</sub>—, m.  $282^\circ$  (82); —CH<sub>2</sub>SO<sub>2</sub>—, m.  $195^\circ$  (90); —(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>—, m.  $260^\circ$  (75); —SO<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>—, m.  $235^\circ$  (decompn.) (75); —SO<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SO<sub>2</sub>—, m.  $208^\circ$  (47); —SO<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>—, m.  $235^\circ$  (decompn.) (80). *Di-NH<sub>2</sub> sulfones*: —SO<sub>2</sub>—, m.  $176.5^\circ$ , yellow (78); —CH<sub>2</sub>SO<sub>2</sub>—, m.  $216^\circ$  (86); —(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>—, m.  $187.5^\circ$ , yellow (73). The above bases were diazotized and coupled with salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid, R-salt, chromotrope,  $\gamma$ -acid, Chicago acid and H-acid and the resulting dyes compared with the corresponding dyes from *p*-MeC<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> and benzidine. C. A. R.

**Arsonation of phenol.** W. G. CHRISTIANSEN AND A. J. NORTON. *J. Am. Chem. Soc.* 45, 2188-92 (1923).—By thoroughly stirring the mixt. of PhOH and H<sub>2</sub>AsO<sub>4</sub> and allowing 1 mol. H<sub>2</sub>O (per mol. PhOH) to distil off before attaching a reflux condenser to the app. the yield of anhyd. *p*-HOC<sub>6</sub>H<sub>4</sub>AsO<sub>3</sub>Na<sub>2</sub> (I) can be increased from the 18-20% obtained by following Jacobs and Heidelberger's directions (C. A. 13, 2371) to 33%. If a reflux condenser is not used after 1 mol. H<sub>2</sub>O has distd. off, about 1 more mol. of H<sub>2</sub>O distills off and the reaction mixt. becomes very tarry, owing to the oxidation of unchanged PhOH or some intermediate substance by the H<sub>2</sub>AsO<sub>4</sub>; I itself gives off no H<sub>2</sub>O and does not form a trace of tar when heated under the same conditions with H<sub>2</sub>AsO<sub>4</sub>. I and the free acid are practically not hydrolyzed at all by distn. with steam, so there is no need of concg. the solns. *in vacuo*, as recommended by J. and H. C. A. R.

**Identification of phenols as 3,5-dinitrobenzoic acid esters.** R. C. BROWN AND R. E. KREMER. *J. Am. Pharm. Assoc.* 11, 607-8 (1922).—Esters of phenol, *o*-, *m*-, and *p*-cresol, guaiacol, carvacrol and thymol were prepd. The m. ps. were, resp.,  $145-6^\circ$ ,  $133-4^\circ$ ,  $180-2^\circ$ ,  $138-9^\circ$ ,  $76-7^\circ$  and  $102-3^\circ$ . L. E. WARREN

**Phenoxy derivatives of propane.** Crystallographic investigation of 1,2-diphenoxyethane and 1,2-diphenoxypropane. G. GUYA. *Bull. soc. chim. Belg.* 31, 245-53 (1922); *Chem. Zentr.* 1923, I, 241-2.—A study of the products obtained by the reaction of equimol. amts. of 25% alc. NaOPh (I) and MeCHBrCH<sub>2</sub>Br (II). I was slowly added to II at  $100^\circ$ , boiled 1-1.5 hrs. and the MeC:CH absorbed in Br-H<sub>2</sub>O. The EtOH and bromopropylene were distd. off, first directly and then by steam distn. until the appearance of PhOH. The steam distillate was fractionated to sep. the EtOH and small amts. of bromopropylene and the residue combined with that from the steam

distn. The PhOH was combined with NaOH, extd. with Et<sub>2</sub>O and the ext. (freed from Et<sub>2</sub>O) rectified *in vacuo*. The residue contained 1,2-diphenoxyethane, whose formation is ascribed to the presence of (CH<sub>3</sub>Br)<sub>2</sub> in the raw material. The wts. given with the compds. obtained are the yields from 12 kg. of II. *1-Phenoxypropylene*, 50 g., m. -63°, b. 180-8°, b<sub>10</sub> 74-6°, d<sub>4</sub><sup>20</sup> 0.9799, n<sub>D</sub> 1.51914, mol. refraction 41.51, unpleasant odor, adds 2 atoms of Br. *2-Phenoxypropylene*, 10 g., b. 170°. *1-Phenoxy-2-bromopropane* and *1-bromo-2-phenoxypropane*, 200 g. together, could not be sepd. on account of similar b. p. The mixt. b. 235-40°, b<sub>10</sub> 115-6°, d<sub>4</sub><sup>20</sup> 1.3553, n<sub>D</sub> 1.54636, mol. refraction 50.26, insol. in H<sub>2</sub>O, yields with alc. KOH 1- and 2-phenoxypropylene. *1,2-Diphenoxypropane*, 150 g., m. 32°, b<sub>10</sub> 175-8°, d<sub>4</sub><sup>20</sup> 1.0748, n<sub>D</sub> 1.53419, mol. refraction 68.00, orthorhombic crystals with a:b:c 0.536195:1:0.619189, insol. in H<sub>2</sub>O. *1,2-Diphenoxyethane*, m. 95°, b. 180-5°, orthorhombic crystals with a:b:c 0.460715:1:1.4518925. MeCH:CHBr and MeBrCH<sub>2</sub>, 5 kg. together. MeC:CH, trace. The rule advanced by Solonina (cf. *J. Russ. Phys.-Chem. Soc.* 30, 826; *Chem. Zentr.* 1899, 1, 248) that dibromides of the type of II give no PhO derivs. with I is therefore incorrect. C. C. DAVIS

A new method of preparation of some aromatic sulfides. I. MICHELLE GIUA AND ANTONIO RUGGERI. *Gazz. chim. ital.* 53, 290-6 (1923). -The method of prep. aromatic sulfides here described consists in a substitution of a labile NO<sub>2</sub> group of aromatic NO<sub>2</sub> derivs. with a S atom by the action of thiourea. When a mixt. of γ-MeC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>) (I) and thiourea in the mol. ratio 1:1 or 3:2 in the presence of EtOH is heated on the H<sub>2</sub>O bath a yellow solid is sepd. composed of 2,4,2',4'-tetranitro-5,5'-dimethyldiphenyl sulfide (II), m. 189-90°, and 2,4,2',4'-tetranitro-5,5'-dimethyldiphenyl disulfide (III), m. 263-5°, which is difficultly sol. in org. solvents. NO<sub>2</sub> is evolved during the reaction, which G. and R. consider consists in the replacement of NO<sub>2</sub> with SC(NH)<sub>2</sub>NH<sub>2</sub> with subsequent transformations which are summarized thus: 6I + 4CS(NH)<sub>2</sub> → 2II + III + 4HCNO + 6H<sub>2</sub>O + 4N<sub>2</sub> + 2NO. The HCNO formed reacts with EtOH, giving H<sub>2</sub>NCO<sub>2</sub>Et or other secondary products which could not be isolated. The presence of EtOH appears to be necessary for the reaction since II and III do not react in CHCl<sub>3</sub>. I treated as above with allylthiourea reacts similarly, giving mainly II. I in EtOH with PhSH reacts thus: 2I + 4PhSH → 2IV + V + 2H<sub>2</sub>O + 2NO. The 2,4-dinitro-5-methyldiphenyl sulfide (IV) thus formed, yellow, m. 142-3°. *Diphenyl disulfide* (V), m. 61-2°. IV with conc. HNO<sub>3</sub> (d. 1.5) in excess dissolved and when poured into H<sub>2</sub>O gave a trinitromethyldiphenyl sulfoxide, m. 203-4°. One g. IV in 50 cc. glacial AcOH, heated with 3 g. CrO<sub>3</sub> at 65-70° for 10 min. and then poured in H<sub>2</sub>O, sepd. 2,4-dinitro-5-methyldiphenyl sulfone, m. 164-5°. III treated with fuming HNO<sub>3</sub> is rapidly dissolved and when poured into H<sub>2</sub>O seps. 4,6-dinitro-*m*-tolylsulfonic acid, m. 120-35°, which was not investigated further. II with HNO<sub>3</sub> (d. 1.5) gives 2,4,2',4'-tetranitro-5,5'-dimethyldiphenyl sulfoxide, m. 260° (decompn.). E. J. WITZEMANN

*p*-Chlorodiphenyl sulfone. HAEHL. *Compt. rend.* 177, 194-5 (1923). -Beckurts and Otto (*Ber.* 11, 2067 (1878)), prep. a chlorodiphenyl sulfone of undetd. constitution by a Friedel and Crafts' reaction of PhSO<sub>2</sub>Cl with PhCl. II. proves the *p*-Cl structure by making the same compd. through sulfanilic acid → *p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>H → ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl → condensation with C<sub>6</sub>H<sub>6</sub>. BEN H. NICOLLET

*N*-Methyl-*p*-amino-*o*-chlorophenol sulfate, a new photographic developer. WALTER G. CHRISTIANSEN. *J. Am. Chem. Soc.* 45, 2192-4 (1923). -2,4-Cl(O,N)C<sub>6</sub>H<sub>3</sub>OH (I), m. 106-8°, is obtained in 11 g. yield from 10 g. *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH in HCl suspension with KClO<sub>3</sub>; 10 g. in boiling H<sub>2</sub>O and a little NaOH with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> gives 5 g. of the NH<sub>2</sub> compd., m. 150-1°, whose HCl salt (II) dissolves very readily in H<sub>2</sub>O with acid reaction to litmus but not to Congo, is oxidized by FeCl<sub>3</sub> with formation of a deep blue color, gives with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>CHO in dil. HCl an orange soln. and an orange ppt., is oxidized and becomes dark brown in alk. soln. From 8.5 g. I in boiling NaOH reduced with Zn, then refluxed with HCHO, filtered into NaHSO<sub>4</sub> soln., treated with concd. HCl until the ppt. first formed redissolves, then with Na<sub>2</sub>CO<sub>3</sub> until the soln. no longer effervesces and extd. with AmOAc, the exts. then being treated with H<sub>2</sub>SO<sub>4</sub>, is obtained 7 g. *N*-methyl-*p*-amino-*o*-chlorophenol sulfate, (C<sub>7</sub>H<sub>5</sub>ONCl)<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub> (III), sol. in H<sub>2</sub>O with acid reaction to litmus, gives a red and then a very deep purple color with FeCl<sub>3</sub> in H<sub>2</sub>O and a white ppt. with NaNO<sub>2</sub> and becomes brown with Na<sub>2</sub>CO<sub>3</sub>. Both II and III are good photographic developing agents; III is the better of the 2 and appears to be equal to, although no better than, Metol. C. A. R.

Temperature of explosion for endothermic substances. II. Trinitro-*m*-cresolates and their explosion temperatures. R. L. DATTA, LOENATH MISRA AND J. C. BARDHAN. *J. Am. Chem. Soc.* 45, 2430-3 (1923); cf. C. A. 14, 226. -Below are the m. ps. and explosion temps., resp., of the addn. compds. of trinitro-*m*-cresol (T) with various



compds. (X): *Acenaphthene*, X. T, yellow, 120°, 451°; *fluorene*, X. T, deep yellow, 109°, 421°; *allylamine*, 3X. T, yellow, 165°, 265°; *benzylamine*, X. T, golden yellow, 185°, 406°; *camphylamine*, X. 2T, lemon-yellow, 183°, 391°; *menthylamine*, X. 2T, lemon-yellow, 200° (decompn.), 410°; *piperazine*, 2X. T, lemon-yellow, 220-5° (decompn.), 359°;  $\alpha$ -C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub>, X. T, dirty yellow, 165-70° (decompn.), 470°; *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, X. 2T, lemon-yellow, 170-2°, 449°; *p*-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, X. 2T, lemon-yellow, 172.5°, 441°; *p*-IC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, X. 2T, bright yellow, 152°, 496°; *o*-MeOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, X. T, pale yellow, 178° (decompn.), 349°; *o*-EtOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, X. T, bright yellow, 165°, 385°; *hexamethylene-tetramine*, X. T, 175°, 325°;  $\psi$ -*cumidine*, X. 2T, yellow, 183° (decompn.), 477°; *triphenylguanidine*, X. T, yellow, 182°, 454°;  $\alpha$ -C<sub>10</sub>H<sub>7</sub>NMe<sub>2</sub>, X. T, 151°, 358°;  $\alpha$ -*naphthol*, X. T, orange-yellow, 159°, 472°;  $\beta$ -*naphthol*, X. T, orange, 124°, 452°. C. A. R.

**Reduction potentials of quinones. I. The effect of the solvent on the potentials of certain benzoquinones.** JAMES B. CONANT AND LOUIS F. FIESER. *J. Am. Chem. Soc.* **45**, 2194-2198(1923); cf. *C. A.* **17**, 14.—To answer the question as to the relationship of the reduction potentials of a series of quinones in different solvents referred to the solid state, these potentials have been measured in alc. and in aq. soln. Essentially the same relationships have been found whether the potentials in aq. or alc. solns. are compared. The potentials referred to the solid state are not entirely parallel to those in soln. From these facts and general considerations it is shown that in comparing the reduction potentials of a series of quinones the substances should ideally be measured in a solvent in which the abs. activity coeff. of the org. substances is 1; alc. and aq. solns. seem to be sufficiently close to this ideal condition to make the measurements in these solvents significant. Benzo-, tolu-, *p*-xylo-, duro-, thymo-, monochloro-, 2,3-, 2,5- and 2,6-dichloro-, trichloro- and tetrachloroquinones were studied. The introduction of alkyl groups progressively lowers, that of Cl at first raises, then lowers, the reduction potential. In order to measure the reduction potential referred to the solid state of those quinones that form quinhydrone it was necessary to measure the potential of cells contg. quinone-quinhydrone and hydroquinone-quinhydrone. The validity of this procedure is demonstrated. Data on the energy of quinhydrone formation have been thus obtained. The temp. coeff. of the reduction potential referred to the solid state has been measured and the total energy of reduction thus calcd. Comparison with previous thermochem. measurements shows great discrepancies in the case of the polychloroquinones, probably owing to the errors inherent in the thermochem. measurements. The data obtained are reported in full. C. A. R.

**Production of thymoquinone on a semi-commercial scale in the laboratory.** R. M. HIXON. *J. Am. Pharm. Assoc.* **11**, 696-700(1922).—Starting with 500 g. of either carvacrol or thymol details are given by which about 430 g. of thymoquinone may be obtained by a modification of the Liebermann-Illinski method. This is 71% of theory. The cost is about \$10.11 per lb. L. B. WARREN

**Amino and oximino derivatives of thymoquinone.** RALPH M. HIXON. *J. Am. Chem. Soc.* **45**, 2333-41(1923).—Quinones, being unsatd. cyclic ketones, should be expected to add NH<sub>2</sub> (or its derivs.) (1) at the C:O group, in analogy with the aldehyde-NH<sub>2</sub> compds., and (2) at the double bond, in analogy with some of the unsatd. aliphatic acids. Evidence that both types of reaction take place is presented. It is also shown that the intermediate addn. compds. between amines and quinones have structures analogous to that of NH<sub>4</sub> salts. Tertiary amines would be expected to form similar addn. compds. which would not rearrange. Thymoquinone dissolves in 2 equivs. PhNMe<sub>2</sub> with considerable absorption of heat; in the absence of solvents and oxidizing agents (including air) the mixt. remains unchanged for months but in their presence is produced a purple tar sol. in acids and decompd. by aq. alkalis; sapon. with 50% H<sub>2</sub>SO<sub>4</sub> gives some di- and the merest trace of monohydroxythymoquinone, which would seem to indicate that actual condensation has taken place just as between quinones and primary or secondary amines. Directions are given for the purification of large amts. (200 g.) of nitrosothymol and -carvacrol; the cryst. compds. discolor very slowly in direct sunlight, whereas the crude products are quite unstable. Their Bz derivs. are converted back into the original nitrosophenols by dry MeNH<sub>2</sub> in heptane at 100°; this reaction, occurring in a H<sub>2</sub>O-free medium, is easily explained if it is assumed that the MeNH<sub>2</sub> adds to the carbonyl O of the Bz group: O=C<sub>6</sub>H<sub>4</sub>RR':NOBz  $\longrightarrow$  O=C<sub>6</sub>H<sub>4</sub>RR':NOCPh(OH)NHMe  $\longrightarrow$  O=C<sub>6</sub>H<sub>4</sub>RR':NOH + BzNHMe. Benzoylnitrosothymol and -carvacrol dropped into concd. HNO<sub>3</sub> form unstable salt-like addn. products, C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>·3HNO<sub>3</sub>, m. 53°, and C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>·2HNO<sub>3</sub>, m. 65°, resp. Thymoquinone dioxime can be obtained in 60-70% yield from nitrosocarvacrol but in only 6-10% yield from nitrosothymol by Kehrman and Messinger's method (*Ber.* **35**, 3557(1902));

its *dibenzoyl*, discolors 170°, m. 190–200°, is obtained practically quant. by the Schotten-Baumann method and is of value for the identification of the dioxime. C. A. R.

**Isomerization of nitro aldehydes by chemical methods.** GUSTAV HELLER. *J. prakt. Chem.* 106, 1–16 (1923).—It is known (*Ber.* 34, 2040; 37, 3430) that *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO (I) in C<sub>6</sub>H<sub>6</sub>, HCN, etc., is transformed by light into *o*-ONC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (II). It is now shown that this O transfer may be caused by purely chem. methods. Ten g. I in 40 g. EtOH, slowly added to 2.1 g. AcONH<sub>4</sub> and 2 g. KCN in 5 g. concd. NH<sub>4</sub>OH with cooling, give 8.5 g. II after 24 hrs. A repetition of the expt. of Beckerantz and Ahlqvist (*C. A.* 5, 288) in which 1.5 g. KCN and 10 g. I stand several hrs. in 50 g. abs. EtOH, gave 3.5 g. II, but no trace of azoxybenzoic acid (III), though III is present if larger amts. of KCN are used. The neutral by product, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>N, m. 162–3°, is formed only in small amts. and is identical with the product, m. 168–9°, found by E. and A. *o*-Nitropiperonal cyanohydrin, pale yellow, m. 119°, results by adding KCN to the NaHSO<sub>3</sub> compd. Dissolved in 5 parts alc. NH<sub>3</sub>, the NH<sub>4</sub> salt of nitroso-piperonylic acid seps. in a few min. The same acid is obtained directly from nitropiperonal by the action of AcONH<sub>4</sub> and KCN in concd. NH<sub>4</sub>OH. 5.2 ClO<sub>2</sub>N<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO, treated with AcONH<sub>4</sub>, KCN and NH<sub>3</sub>, gives 5.2 ClO<sub>2</sub>N<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H. The corresponding *5-bromo acid*, pale brown, m. 173°. 2.4 (O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO gives 2.4 ON(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H. 2-Nitro-4-nitrosobenzoyl acid, yellow, m. 230° (decompn.), from 1 g. (O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO in 4 g. AcOH, treated with 0.5 g. KCN in 1 cc. H<sub>2</sub>O. PhNHNH<sub>2</sub> gives a salt, m. 163° (decompn.), decompd. by Na<sub>2</sub>CO<sub>3</sub>. *Me ester*, yellow, m. 141°. *o*-Nitrophenylacetyl nitrile (IV), O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(OH)CN, m. 70–1°, from *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CHO and KCN. No NH<sub>4</sub> salt results upon treatment with alc. NH<sub>3</sub> and upon addn. of HCl a dark oil seps. *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO also gives only resinous products. IV is saponif. by 75% H<sub>2</sub>SO<sub>4</sub> to the amide, m. 195°, and this in turn by AcOH and concd. HCl to *o*-nitrophenylacetic acid, m. 72°, which, with Zn dust and concd. HCl, yields 3-hydroxyhydrocarboxystiril. *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH(OH)CHO does not yield a NO deriv. with KCN and AcONH<sub>4</sub> in NH<sub>4</sub>OH. *o*-Nitrocamphenylglyoxyl nitrile, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CHCH(OH)CN, m. 79°. Alc. NH<sub>3</sub> splits off HCN, forming a resin. 2-Chloro-5-nitromandelyl nitrile, m. 124°. The action of NH<sub>4</sub>CN gives a compd. m. 303°. C. J. WEST

**Simplification of the Gattermann synthesis of hydroxy aldehydes.** ROGER ADAMS AND I. LEVINE. *J. Am. Chem. Soc.* 45, 2373–7 (1923). The disagreeable features connected with the use of HCN in the Gattermann synthesis of HO aldehydes can be avoided by using Zn(CN)<sub>2</sub> instead of HCN. A Zn(CN)<sub>2</sub> suitable for this purpose can be prepd. by pptg. the impurities (NaOH and Na<sub>2</sub>CO<sub>3</sub>) from aq. com. NaCN with MgCl<sub>2</sub> and then pptg. the Zn(CN)<sub>2</sub> with 1 mol. ZnCl<sub>2</sub> in alc.; the product contains about 90% Zn(CN)<sub>2</sub> and contains no impurities which will interfere with the synthesis. If kept in a dry atm. it apparently decomp. only very slowly; after several weeks it shows a depreciation of only about 2%. Into 20 g. of the phenol in 150–200 cc. dry Et<sub>2</sub>O and 1.5 mols. Zn(CN)<sub>2</sub> in a bottle provided with a stirrer and a reflux condenser HCl gas is passed until all the phenol has reacted (about 2 hrs.), the Et<sub>2</sub>O is decanted off and the imide-HCl salt decompd. with H<sub>2</sub>O or dil. alc. In this way were obtained 95% of resorcyaldehyde, m. 135–6°, 85% of orcinolaldehyde, m. 178–80°, 85% of β-naphthalaldehyde, m. 80–1°, 72% of α-naphthalaldehyde, m. 178°, and 45% of pyrogallolaldehyde, m. 158°. C. A. R.

**Aryl-1,3-benzodioxanes (arylmethylenesaligenins).** ROGER ADAMS, A. W. SLOAN AND B. S. TAYLOR. *J. Am. Chem. Soc.* 45, 2417–20 (1923); cf. *C. A.* 16, 1941.—The condensation of saligenin (I) with aromatic aldehydes to form 1,3-benzodioxanes is a general reaction and takes place with the greatest ease; with the substituted compds. no catalyst is necessary. The 2-aryl-1,3-benzodioxanes, which are obtained in 60–95% yield, are cryst. compds. very stable towards alkalis but decompd. by acids into their components. The following compds. were prepd.: C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Cl, from I and *p*-ClC<sub>6</sub>H<sub>4</sub>CHO, m. 107–7.5°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br, from *p*-BrC<sub>6</sub>H<sub>4</sub>CHO, m. 117–7.5°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N, from *m*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO, m. 88–9.5°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br, from 5,2-Br/HO-C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>OH (II) and BzH, m. 85°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>BrCl, from II and *p*-ClC<sub>6</sub>H<sub>4</sub>CHO, m. 147–8°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br, from *p*-BrC<sub>6</sub>H<sub>4</sub>CHO, m. 143–4°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br, from II and PhCH<sub>2</sub>CHCHO, m. 118–20°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>, from 5,2-Me(HO)C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>OH (III), and BzH, m. 90°; C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br, from III and *p*-BrC<sub>6</sub>H<sub>4</sub>CHO, m. 130°. II, m. 107–9°, was obtained in 41 g. yield from I with 1 mol. Br water at 5–10°, and III, m. 105°, quant. from Me(HO)C<sub>6</sub>H<sub>3</sub>CHO in alc. with Pt oxide and a little FeCl<sub>3</sub> (*C. A.* 17, 2277). C. A. R.

**The polarimetric estimation of acid and basic groups in various types of compounds.** I. The estimation of basic groups. J. GROOT. *Biochem. Z.* 137, 517–30 (1923).—A modification of the Waterman procedure is described (cf. *C. A.* 12, 685). The NH<sub>2</sub> group of anthranilic acid neutralizes 1 equiv. of acid. GEORGE ERIC SIMPSON

***o*-Hydroxyquinoline derivatives from the *N*-benzal compounds of *o*-aminophenylacetic acid?** A. KLINGL AND ADOLF SCHMALLENBACH. *Ber.* 56B, 1517-20(1923).—Starting with  $o\text{-HO}_2\text{CC}_6\text{H}_4\text{NHN:CHR}$  (I) ( $R = \text{Ph}$ , *o*- and *m*- $\text{C}_6\text{H}_4\text{NO}_2$  and  $o\text{-C}_6\text{H}_4\text{Cl}$ ), all attempts to obtain compds. of the type  $\text{C}_6\text{H}_4\text{NH.N:CR.CO}$  by intramol. elim-

ination of  $\text{H}_2\text{O}$  by heating with acids or treating with dehydrating agents failed, whereas according to Neber (*C. A.* 16, 3474)  $o\text{-HO}_2\text{CCH}_2\text{C}_6\text{H}_4\text{N:CHR}$  (II) ( $R = o\text{-C}_6\text{H}_4\text{NO}_2$ ) on heating loses  $\text{H}_2\text{O}$  with formation of  $\text{C}_6\text{H}_4\text{N:CR.CO.CH}_3$  or  $\text{C}_6\text{H}_4\text{N:CR.C(OH):CH}$ .

The compds. I and II are capable of existing in *cis*- and *trans*-forms and it seemed possible that the differing behavior of K. and S.'s substances on the one hand and N.'s on the other might be due to the fact that the former have the *trans*-form (H of the CHR group away from the  $\text{CO}_2\text{H}$ ) and the latter has the *cis*-form. To test this point efforts were made to close the ring in *o*-pyrrolhydrazinobenzoic (*o*-methylglyoxalhydrazinobenzoic) acid,  $\text{HO}_2\text{CC}_6\text{H}_4\text{NHN:CHAc}$  (III), which, according as it has the *trans*-form (H of the CHAc away from the  $\text{CO}_2\text{H}$ ) or *cis*-form (H next to the  $\text{CO}_2\text{H}$ ), should lose  $\text{AcOH}$  or  $\text{H}_2\text{O}$ , with formation of  $\text{C}_6\text{H}_4\text{NH.N:CH.CO}$  or  $\text{C}_6\text{H}_4\text{NH.N:CAC.CO}$ , resp.

Here again, all such attempts failed, which makes it improbable that it is due to spatial relations that  $\text{H}_2\text{O}$  cannot be eliminated from the I. Now, when II is heated so cautiously that there is no or hardly any evolution of steam and the cooled melt is taken up in  $\text{Et}_4\text{O}$ , considerable  $o\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  can be extd. from the  $\text{Et}_4\text{O}$  with aq.  $\text{NaHSO}_3$  (0.3 g. of its phenylhydrazone from 1 g. II, corresponding to a 27.7% decompn. of the II); the other product of the decompn. can be only oxindole. A blank expt. on unheated II showed that the decompn. was not effected by the  $\text{NaHSO}_3$  and  $\text{Et}_4\text{O}$ . On the other hand, the decompn. occurs to a considerable extent when II is boiled about 10 min. in xylene. Furthermore, equal parts of oxindole and  $o\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  heated 15 min. at  $120^\circ$  give the compd. m.  $226\text{--}7^\circ$  obtained by N. by heating II; this is therefore not a hydroxyquinoline or a quinolone, as he believed, but 3-*o*-nitrobenzaloxindole. III, yellow, begins to sinter slightly above  $200^\circ$ , decompn. around  $215^\circ$ , is readily prepd. from  $\text{AcCH}_2\text{CO}_2\text{Et}$  allowed to stand 24 hrs. in KOH, acidified and treated with diazotized  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ ; *osazone*,  $\text{HO}_2\text{CC}_6\text{H}_4\text{NHN:CHC(=NNHPh)Me}$ , yellow, turns brown above  $200^\circ$ , m. around  $215^\circ$  (decompn.), becomes red-yellow in contact with concd. HCl but regains its pure yellow color in the air, decompn. in boiling  $\text{AcOH}$  into  $\text{PhNH}_2$  and 1-*o*-benzoic acid]-3-methylsotriazole, darkens about  $240^\circ$ , m. around  $275^\circ$  (decompn.). C. A. R.

**Absolute asymmetric syntheses.** G. BREDDIG, P. MANGOLD AND TH. G. WILLIAMS. *Z. angew. Chem.* 36, 456-8(1923); cf. *C. A.* 4, 2066; Bredig, *Ullmann Enzyklo. Techn. Chem.* VI, 678(1919).—From previous work it seems that an essential prerequisite for proper conditions in asym. synthesis is a knowledge of the changes in the dielec. consts. of the system. As a preliminary study, the dielec. consts. and the cond. of anhyd. HCN and  $\text{PhCH(OH)CN}$  were measured to det. if by the synthesis of the latter from BzH and HCN the dielec. consts. were appreciably changed. The sp. cond. of the purest sample of HCN was found to be  $0.46 \times 10^{-4}$  reciprocal ohms at  $0^\circ$  and  $1.1 \times 10^{-4}$  at  $21^\circ$  (cf. Schlundt, *J. Phys. Chem.* 1901, 503); for BzH,  $1.6 \times 10^{-4}$  at  $0^\circ$  (cf. Walden, *Z. physik. Chem.* 46, 149(1903)); for  $\text{PhCH(OH)CN}$   $1.63 \times 10^{-4}$  at  $0^\circ$  and  $5.91 \times 10^{-4}$  at  $23.5^\circ$ . The dielec. consts. (D) were detd. and found to be (cf. Nernst, *Z. physik. Chem.* 14, 622(1894); Turner, *Ibid* 35, 385(1900)):  $\text{H}_2\text{O}$ ,  $D_{20}$  80.5;  $\text{PhNO}_2$ ,  $D_{20}$  35.9; BzH,  $D_{20}$  17.7,  $D_{25}$  18.6;  $\text{PhCH(OH)CN}$ ,  $D_{20}$  26.2;  $D_{25}$  27.5; HCN,  $D$  227, 219, 205, 180, 171, 165, 156, 132, 123, 114 at  $-13.5^\circ$ ,  $-12.1^\circ$ ,  $-10.5^\circ$ ,  $-5.8^\circ$ ,  $-3.0^\circ$ ,  $-1.0^\circ$ ,  $1.6^\circ$ ,  $10.2^\circ$ ,  $15.6^\circ$ ,  $22.1^\circ$ , resp. These results indicate that the dielec. consts. of the system are greatly changed in the formation of  $\text{PhCH(OH)CN}$  from HCN and BzH particularly at low temps. and that a higher electrostatic field would exert an influence in the asym. synthesis of the optical isomers. *Diasocamphor* (I), prepd. from inactive as well as that (II) from *d*-aminocamphor is decompd. in  $\text{PhH}$  by the action of light with a wave length of  $\lambda$  220-300 $\mu$ . Visible light has almost no action. II is more rapidly decompd. during the first interval of exposure, indicating an active dextro-intermediate decompn. product. I was exposed at  $19^\circ$  to circularly polarized light for 14 weeks without change in optical activity. Inactive lactic acid exposed 6 weeks to light of  $\lambda$  220-290 $\mu$  lost  $\text{CO}_2$  but remained unchanged in optical activity. With light of  $\lambda$  220-300 $\mu$  [ $\text{Coen}_2\text{Cl}$ ]<sub>2</sub> was unchanged, 1,2-*cis* [ $\text{Coen}_2\text{Cl}_2$ ]<sub>2</sub> was very unstable but fairly stable to

larger  $\lambda$  values; [ $\text{Coen}_2\text{NH}_2\text{Cl}$ ]<sub>2</sub> and [ $\text{en}_2\text{Co}$ ]<sub>2</sub> were moderately

affected and much less with large  $\lambda$  values. The last three salts with asym. arrangements were readily decompd. by circularly polarized light of  $\lambda$  250 $\mu$ , but in no case was a trace of optical change observed. N. A. LANGE

**Action of bromine on methylcoumaric and methylcoumarinic acids.** EBNAR BILMANN AND HAKON LUND. *Ann. chim.* 18, 263-82(1922).—Methylcoumaric acid (I) and methylcoumarinic acid (II) are, resp., *trans*- and *cis*-forms; II is dimorphous, m. 86°, or 93.6°. Either I or II, treated with Br<sub>2</sub> in CCl<sub>4</sub>, gives but a single dibromide (III) (yield 85-95%), m. 175°, either in sunlight or in darkness; it is reconverted quant. to I by boiling with Zn powder in alc. III is hydrolyzed by H<sub>2</sub>O to *o*-MeOC<sub>6</sub>H<sub>4</sub>CH(OH)CHBrCO<sub>2</sub>H (IV) (yield 65-70%), m. 134°, crystals from H<sub>2</sub>O with 1H<sub>2</sub>O. IV can easily give III when heated with HBr in AcOH, or be dehydrated to the known  $\alpha$ -bromo- $\beta$ -*o*-anisylacrylic acid by heating with NaOAc in AcOH; it also gives I when heated with alc. and Zn. Steam passed through III gave a distillate contg. *o*-methoxystyryl bromide, oil, b<sub>10</sub> 142-3°. A soln. of III in Br<sub>2</sub> water, gave the 5-Br deriv. (VI) of IV, dimorphous, m. 137°, resolidifying and m. 153.4°; the latter is the stable form. In the case of VI, and other compds. brominated in the nucleus, the structure was proven in each case by oxidation with KMnO<sub>4</sub> to 5,2-Br(MeO-C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H). Somewhat similarly, III gave an  $\alpha$ , $\beta$ , $\delta$ -Br<sub>3</sub> deriv. (VII), m. 197° (Perkin, *J. Chem. Soc.* 39, 422 (1881) gave 185-8°), also obtained from VI and HBr in AcOH. On passing steam for some time into VII, VI was obtained, m. 154°. II, heated in H<sub>2</sub>O with Hg(OAc)<sub>2</sub>, gave *o*-MeOC<sub>6</sub>H<sub>4</sub>CH(OH)CH<sub>2</sub>CO<sub>2</sub>H, which, treated with H<sub>2</sub>S, yielded  $\beta$ -hydroxydi-

*hydromethylcoumaric acid* (VIII), in 60% yield, m. 88.5°; VIII, heated with dil. H<sub>2</sub>SO<sub>4</sub>, gave I. Bromination of VIII in H<sub>2</sub>O gave the 5-Br deriv., m. 108°. Oxidation of I with KMnO<sub>4</sub> gave *o*-MeOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 101.5° (previously reported, m. 98-9°); on bromination this acid gave the 5-Br deriv., m. 120-0.5°, instead of 119°, as previously reported. BEN H. NICOLET

**The separation of optical isomers by distillation and crystallization.** G. DUPONT AND H. DESALBRES. *Compt. rend.* 176, 1881-4(1923).—Report of the successful sepn. by distn. in a special app. and by fractional crystn. of active *pinene* from the inactive mixt. (not racemic) of the optical opposites. G. L. CLARK

**Action of phosphorus pentachloride on pinene.** LEONCE BERT. *Bull. soc. chim.* 33, 787-90(1923).—Naudin (*Bull. soc. chim.* [2] 37, 111(1883)) passed 1 mol. dry Cl<sub>2</sub> into pinene (I) containing 4% PCl<sub>5</sub>, and claimed a yield of 75% *cymene* (II). B. obtained by this method only traces of II, but an increase as the original PCl<sub>5</sub> was increased. PCl<sub>5</sub> and I react rather vigorously at room temp., evolving more HCl than would be required if II were the sole product. After rather complex manipulation of the distn. products were isolated 13% I, some unaltered II, some 20% of colophene, C<sub>10</sub>H<sub>16</sub>, b. 300-30°, and, from lower fractions, (210-30°) a *pinene dichloride*, m. 183°, and a less pure liquid isomer. These last two products are considered as probably identical with similar ones described by Aschan (*C. A.* 15, 1494). BEN H. NICOLET

**The action of phenylhydrazine on pinene nitrosochloride.** R. E. KREHMERS. *J. Am. Pharm. Assoc.* 11, 604-6(1922).—PhNHNH<sub>2</sub> and pinene nitrosochloride were allowed to react in 95% EtOH. Three fractions were obtained: (1) PhNHNH<sub>2</sub>·HCl; (2) yellowish crystals, m. 147-8°, readily sol. in EtOH, unidentified; (3) faintly yellowish, hard prisms, m. 148-50°; analysis indicated C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>. L. E. WARREN

**Molecular rearrangements of the camphor series.** XIV. Structure of isocampholactone. P. K. PORTER WITH W. A. NOYES. *J. Am. Chem. Soc.* 45, 2366-73(1923).—Isocampholactone (I) is shown to be 3-hydroxy-1,2,3-trimethylcyclopentanecarboxylic lactone. I (65 g.) heated 72 hrs. with HNO<sub>3</sub> (d. 1.27) gives 40 g. of the NO<sub>2</sub> deriv. (II), m. 121-2°, and 11.7 g. of 3-hydroxy-1,2-dimethylcyclopentanedicarboxylic acid lactone (III), m. 138-8°; this, heated 24 hrs. with the calcd. amt. of NaOH and treated with AgNO<sub>3</sub>, gives 90.5% of the *di*-Ag hydroxydicarboxylate, which in Et<sub>2</sub>O with MeI yields 87.8% of the *di*-Me ester, b<sub>10</sub> 156-60°, this with Beilmann's CrO<sub>3</sub> mixt. gives only a slight darkening even after 12 hrs., showing that the HO group is tertiary. Heated 5 min. with PCl<sub>5</sub>, freed from the POCl<sub>3</sub> in *vacuo* and treated in Et<sub>2</sub>O with cold concd. NH<sub>4</sub>OH, III yields 75% of a 3-amide, m. 162-3°, 2.02 g. of which in 10% NaOH with NaOBr gives an oily 3-keto-1,2-dimethylcyclopentanecarboxylic acid (yield, 1.85 g. of the Ba salt, (C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>)<sub>2</sub>Ba·2H<sub>2</sub>O), the acid with 2 mols. MeMgI gives I and an acid, m. 96-7°, [ $\alpha$ ]<sub>D</sub> -37.5° (0.1681 g. in 5 cc. abs. alc.), which is probably the *trans*-HO acid. II with concd. NH<sub>4</sub>OH gives 83% of 2-nitro-1-methylcyclobutanecarboxamide, m. 94-5°, while with warm 2 N NaOH is obtained 80-100% of the free acid, (IV) (isolated as the Ba salt, (C<sub>8</sub>H<sub>10</sub>NO<sub>3</sub>)<sub>2</sub>Ba·2.5H<sub>2</sub>O), m. 70-2°, [ $\alpha$ ]<sub>D</sub> -101.51°, -246.81°, -119.3°, -87.31° for the 546.1, 578, 435 and D lines at 25°; Ag salt, b<sub>10</sub> 120-5° (some

decompn.),  $[\alpha] -80.2^\circ$ ,  $-93.2^\circ$  for the 578.1 and 546.1 lines at  $25^\circ$ ,  $d_{20} 1.16907$ ,  $n 1.4416$ . IV, its amide and ester with  $\text{HNO}_3$  give the blue color characteristic for sec.  $\text{NO}_2$  groups. The amide with 1 mol.  $\text{NaOEt}$  in abs. alc. quant. yields a *Na salt*,  $\text{C}_8\text{H}_7\text{N}_2\text{O}_3\text{Na}$ , hydrolyzed to IV by dil.  $\text{H}_2\text{SO}_4$ ; with 2 mols. of hot 10%  $\text{NaOH}$  and subsequent acidification is obtained a blue color which disappears on warming;  $\text{N}_2\text{O}$  is evolved and IV is formed. The ester likewise gives an unstable *Na salt* which on hydrolysis with  $\text{H}_2\text{SO}_4$  yields a blue soln., evolves  $\text{N}_2\text{O}$  and  $\text{CO}_2$  and gives IV. From the volatile products of the decompn. of II by  $\text{NaOH}$  was isolated 60%  $\text{Me}_2\text{CO}$ .

C. A. R.

**Xanthate method in the fenchene and isofenchene series.** S. S. NAMEYKIN, A. SELIVANOV AND A. RUZHENTZEV. *J. prakt. Chem.* 106, 25-38(1923); cf. C. A. 11, 583.—A specially pure *fenchyl alc.* (I),  $b_{760} 200-0.5^\circ$ ,  $m. 49^\circ$ ,  $[\alpha]_D -10.9^\circ$ , is obtained from the high boiling fraction of the dehydration product of I, after purification through the *Na acid phthalate*; the *acid ester*,  $m. 146.5^\circ$  and has  $[\alpha]_D 23.23^\circ$ . The steric configuration of I corresponds to borneol, while the oily product removed in the above treatment probably corresponds to isborneol. Heating *fenchyl Et xanthate* to  $150-230^\circ$  gave a mixt. of hydrocarbons,  $b_{747} 146-8^\circ$ ,  $d_{20}^{20} 0.8636$ ,  $n_{20} 1.4579$ ,  $[\alpha]_D -12.3^\circ$ . Treatment with  $\text{KMnO}_4$  followed by distn. over  $\text{Na}$ , reduced 18 g. of this product to 4 g. of a hydrocarbon identical with the cyclofenchene of Aschan (C. A. 6, 1144),  $b_{747} 143-3.5^\circ$ ,  $d_{20}^{20} 0.8609$ ,  $n_{20}^{20} 1.4532$ ,  $[\alpha]_D -1.77^\circ$ . The oxidized portion consists of *d,l*-fenchene, since *d,l*-hydroxyfenchenic acid,  $m. 154-5^\circ$ ,  $[\alpha]_D -37.42^\circ$ , is isolated from the aq. soln. *Isofenchyl alc.* (purified through the *Me xanthate amide*,  $m. 69-70^\circ$ ,  $[\alpha]_D -37.77^\circ$ ,  $m. 60.5-1^\circ$ ,  $[\alpha]_D -27.04^\circ$ . Fenchylene was prepd. from the *Me xanthate*, the solid amide and the liquid amide (probably mixed with ester); that from the solid amide  $b_{740} 140-1^\circ$ ,  $d_{20}^{20} 0.8397$ ,  $n_{20} 1.4502$ ,  $[\alpha]_D -57.28^\circ$  ( $\text{EtOH}$ ,  $p 6.5\%$ ); the other preps. showed very similar properties, but they are not identical, there being an impurity present of higher b. p., d. and  $n$ , but with lower optical activity. The action of  $\text{Br}$  upon fenchylene gives a heavy oil, which did not cryst.  $\text{EtNO}_2$  in  $\text{AcOH}$  gives a *nitrosyl chloride*,  $m. 131^\circ$ . Oxidation with 1%  $\text{KMnO}_4$  gives *cis*-fenchocamphoric acid.

C. J. WEST

**Isofenchocarboxylic acid.** S. NAMEYKIN AND A. RUZHENTZEV. *J. prakt. Chem.* 106, 39-40(1923).—Isofenchone in dry  $\text{Et}_2\text{O}$  is treated with dry  $\text{CO}_2$  in the presence of  $\text{Na}$  wire; after the vigorous reaction has moderated, the mixt. is heated 3 days. The by-products, isofenchone and isofenchyl alc., are removed with  $\text{Et}_2\text{O}$  and the salt was decompd. with dil.  $\text{H}_2\text{SO}_4$ . *Isofenchocarboxylic acid*,  $m. 87-8^\circ$  ( $\text{CO}_2$  evolution), gives a dark blue color with  $\text{FeCl}_3$ , changing to a dirty gray, and decomp. upon standing in the dark, yielding isofenchone and a *compd.*,  $m. 230-1^\circ$  (decompn.). The amt. was too small to study.

C. J. WEST

**Formation of free radicals by reduction with vanadous chloride (preliminary paper).** J. B. CONANT AND A. W. SLOAN. *J. Am. Chem. Soc.* 45, 2466-72(1923).— $\text{VCl}_2$  ppts. from solns. of triphenylpyrylium chloride a reddish substance which can be obtained fairly pure by filtering in  $\text{CO}_2$  and which behaves like a free radical; it dissolves in  $\text{CHCl}_3$  with a bright red color which disappears on shaking with air;  $\text{FeCl}_3$  oxidizes it back to the pyrylium salt, 1 mol. of the  $\text{FeCl}_3$  being required if the process is carried out in the absence of  $\text{O}$  (if the ppt. has stood for some hrs., even in  $\text{CO}_2$ , considerably less than 1 mol.  $\text{FeCl}_3$  is required). Similarly phenylxanthanol in concd.  $\text{HCl}$  with  $\text{VCl}_2$  gives a brown ppt. sol. in  $\text{C}_6\text{H}_6$  with a red color identical to the *eye* with that produced by phenylxanthyl prepd. by Gomberg's method from the chloride with metals in  $\text{C}_6\text{H}_6$ ; furthermore, with air this soln. gives phenylxanthyl peroxide. Likewise,  $\text{Ph}_3\text{COH}$  in very concd. aq.  $\text{ZnCl}_2$  satd. with  $\text{HCl}$  gives with  $\text{VCl}_2$  a colored ppt. contg.  $\text{Ph}_3\text{C}$ , as shown by the color of the  $\text{C}_6\text{H}_6$  soln. and the formation of the peroxide; in concd.  $\text{H}_2\text{SO}_4$  also,  $\text{Ph}_3\text{COH}$  gives with  $\text{VCl}_2$  a ppt. contg.  $\text{Ph}_3\text{C}$ . A very dil. soln. of xanthanol in cold concd.  $\text{HCl}$  immediately gives with  $\text{VCl}_2$  a pink ppt. which is stable for a few hrs. in the air but gradually changes into the colorless bixanthyl; it dissolves in  $\text{CHCl}_3$  in the absence of air with a faint red color which disappears in a few sec. and evapn. of the soln. yields bixanthyl. When aq. benzylpyridinium chloride is treated with 1.5 times the amt. of  $\text{VCl}_2$  equiv. to 2 atoms of  $\text{H}$  no ppt. is formed but the  $\text{VCl}_2$  is evidently oxidized, as the 1st portion of it rapidly changes color, and on making the soln. strongly alk. and extg. the resulting suspension with  $\text{Et}_2\text{O}$  and evapn. the ext.  $N,N'$ -dibenzyltetrahydropyridyl is obtained; by analogy, there is every reason for believing that the 1st step in the process is the formation of free benzylpyridinium, which, being sol. in the acid soln., immediately polymerizes to the bimol. form.

C. A. R.

**Benzil rearrangement. V. Cannizzaro's reaction.** ARTHUR LACHMAN. *J. Am.*

*Chem. Soc.* 45, 2356-63 (1923); cf. *C. A.* 17, 2421.— $\text{PhCH}_2\text{OBz}$  (I) is formed from  $\text{BzH}$  and  $\text{NaOH}$  even in the presence of  $\text{H}_2\text{O}$  if precautions are taken to prevent its subsequent hydrolysis (avoidance of an excess of alkali and prevention of any considerable rise in temp.). Thus, 106 g.  $\text{BzH}$  shaken in a tightly stoppered flask with 0.1-0.5 mol. of 10-19  $\text{N}$   $\text{NaOH}$  for 2-96 hrs. gives 1-12 g. I and 1-35 g.  $\text{BzOH}$ ; in some cases nearly 0.5 of the total amt. of  $\text{BzOH}$  produced can be isolated as I. Alkalies convert  $\text{PhCH}_2\text{OH}$  into  $(\text{PhCH}_2)_2\text{O}$  (II); 50 g. of the alc. heated 4 hrs. on the  $\text{H}_2\text{O}$  bath with 25 cc. of 10  $\text{N}$   $\text{NaOH}$  gives 0.9 g. II. This dehydration may occur without any catalyst at all other than the walls of the vessel; 30 g. of the alc. heated 5 days at  $210-5^\circ$  in a sealed tube gave 2 g.  $\text{H}_2\text{O}$ , 6 g. unchanged alc., 3 g. II and 17 g. of decompn. products of II (6.9 g.  $\text{PhMe}$ , 6.1 g.  $\text{BzH}$ , 3.8 g. high boiling residue). From 30 g. II similarly treated were obtained 8.5 g.  $\text{PhMe}$ , 7.5 g.  $\text{BzH}$ , 8 g. unchanged II and 5.5 g. high boiling residue, the main reaction being  $\text{II} = \text{PhMe} + \text{BzH}$ .  $\text{PhCH}_2\text{OH}$  (30 cc.) heated 45 hrs. at  $150^\circ$  with 2 g.  $\text{Na}$  gives 0.9 g.  $\text{BzOH}$ , 1.4 g. II and 1.2 cc.  $\text{PhMe}$ ;  $\text{PhCH}_2\text{OH} + \text{PhCH}_2\text{ONa} = \text{II} + \text{NaOH}$ , the II undergoing metaklyny (oxidation-reduction) with formation of  $\text{PhMe}$  and  $\text{BzH}$  and the latter finally yielding  $\text{BzOH}$  by the Cannizzaro reaction. II (48 g.) slowly treated with 80 g.  $\text{Br}$ , distd. and treated with  $\text{Na}_2\text{CO}_3$  yields 32 g.  $\text{PhCH}_2\text{Br}$  and 36 g.  $\text{BzOH}$ ;  $\text{II} + 2\text{Br}_2 = \text{PhCH}_2\text{Br} + \text{BzBr} + 2\text{HBr}$ . From 45 g. of the so-called "bromobenzyl benzoate" (III) (formed by addn. of  $\text{PhCH}_2\text{Br}$  to  $\text{BzH}$ ) allowed to stand in cold abs. alc. until dissolved and then treated with a slight excess of  $\text{Na}_2\text{CO}_3$  are obtained 15.9 g.  $\text{BzH}$ , 8.8 g.  $\text{BzOEt}$  and 11.8 g.  $\text{BzOH}$ , indicating that III really has the structure  $\text{BzOCH}_2\text{BrPh}$ . The above facts afford definite proof that I is an intermediate product in the Cannizzaro reaction, the mechanism of which may probably be represented by the following equations:  $\text{PhCH}(\text{OR})(\text{ONa}) + \text{BzH} = \text{PhCH}(\text{OR})\text{OCH}(\text{ONa})\text{Ph}$ ;  $\text{PhCH} + \text{OCH}(\text{OR})(\text{ONa})\text{Ph} = \text{PhCH}_2\text{OC}(\text{OR})(\text{ONa})\text{Ph} = \text{I} + \text{NaOR}$ . Below are a few general rules which seem to apply to the field covered in this series of papers: (1) HO groups attached to 2 neighboring C atoms ( $\alpha$ - or  $\beta$ -position) rearrange to form a C:O group with loss of  $\text{H}_2\text{O}$ . (2) A single HO group, at least in primary alcs., tends to form a C:O group (aldehyde). (3) The CO group tends to add HO or RO and pass over into  $\text{CO}_2\text{H}$  or  $\text{CO}_2\text{R}$ . (4) The readjustment of CO to  $\text{CO}_2\text{H}$  necessarily involves the severance of a C—C bond; this may occur by rupture, producing 2 smaller mols., or by rearrangement of the C chain; other things being equal, the latter seems to be preferred. (5) The preference for rearrangement over rupture also applies to reactions under (1).

C. A. R.

**The two methylnaphthalenes. I.  $\alpha$ -Methylnaphthalenesulfonic acids.** K. ELBS AND BR. CHRIST. *J. prakt. Chem.* 106, 17-24 (1923).— $1\text{-C}_{10}\text{H}_7\text{Me}$  (140 g.) and 250 g. concd.  $\text{H}_2\text{SO}_4$ , shaken for 5-6 hrs. until the mixt. is half solid, then dissolved in  $\text{H}_2\text{O}$ , filtered, neutralized with  $\text{BaCO}_3$  and again filtered, gives a very good yield of the *Ba 1-methylnaphthalenesulfonate*, leaflets with 1  $\text{H}_2\text{O}$ , lost at  $130-5^\circ$ , sol. in about 90 parts  $\text{H}_2\text{O}$  at room temp. The free acid is deliquescent, very sol. in  $\text{H}_2\text{O}$  and easily sol. in concd.  $\text{H}_2\text{SO}_4$ . The constitution was established by the transformation into 1,4-MeC<sub>10</sub>H<sub>6</sub>OH. Cu salt, bluish green, with 4 mols.  $\text{H}_2\text{O}$ , lost at  $135^\circ$ . One part anhyd. salt dissolves in 46 parts  $\text{H}_2\text{O}$  at room temp. The K and Na salts are not characteristic. Attempts to oxidize the Me group with  $\text{KMnO}_4$  failed. The sulfonyl chloride, m.  $81^\circ$ , is obtained in 90-5% yield from the Na salt and  $\text{PCl}_5$  by heating 2 hrs. on the  $\text{H}_2\text{O}$ -bath. Amide, m.  $174^\circ$ . Hydrazide, m.  $124-5^\circ$  (decompn.); the compd. is quickly decompd. by boiling  $\text{H}_2\text{O}$  and reduces  $\text{NH}_4\text{OH-Ag}_2\text{O}$  in the cold. The Ac deriv., m.  $220-2^\circ$  (decompn.), is more stable. Anilide, m.  $158^\circ$ . Me ester, from the chloride and  $\text{MeOH}$  or the Na salt and  $\text{Me}_2\text{SO}_4$ , m.  $107^\circ$ . Et ester, needles, m.  $98^\circ$ . The chloride is reduced by Zn in boiling  $\text{H}_2\text{O}$  to 1,4-methylnaphthalenesulfonic acid, m.  $114-5^\circ$ . The concd.  $\text{H}_2\text{SO}_4$  soln. is deep violet, changing to a dirty green. Na salt, leaflets with 3  $\text{H}_2\text{O}$ ; Cu salt, pale green insol. ppt. When 10 g. of chloride, 20 g. Fe wire, 40 cc.  $\text{H}_2\text{O}$  and 60 cc. concd.  $\text{HCl}$  are heated 6 hrs. the mercaptan, 1,4-MeC<sub>10</sub>H<sub>6</sub>SH, yellow oil,  $b_n$   $168-78^\circ$ , results, analyzed as the yellow Pb salt. The Hg compd. is pale yellow. Allowed to stand 2 days in alc.  $\text{NH}_3$ , 1,1'-dimethyldinaphthyl 4,4'-disulfide, m.  $114^\circ$ , is formed. 1,4-MeC<sub>10</sub>H<sub>6</sub>OH is obtained in 30-40% yield upon fusion of 10 g.  $\text{MeC}_{10}\text{H}_7\text{SO}_3\text{Na}$ , 50 g. KOH and 10 cc.  $\text{H}_2\text{O}$ .

C. J. WEST

**Trihydroxymethylanthraquinones.** I. G. D. GRAVES WITH ROGER ADAMS. *J. Am. Chem. Soc.* 45, 2439-55 (1923).—1,4,2,3-C<sub>14</sub>H<sub>8</sub>(OMe)<sub>2</sub>(CN)<sub>2</sub>, m.  $275^\circ$  (all m. ps. are cor.), obtained in 85% yield from the di-HO compd. with  $\text{Me}_2\text{SO}_4\text{-KOH}$ , gives with concd.  $\text{H}_2\text{SO}_4$  on the  $\text{H}_2\text{O}$  bath 64% 3,6-dimethoxyphthalic anhydride (I), m.  $259-61^\circ$ , 10 g. of which with  $\text{AlCl}_3$  and *p*-cresol at  $70^\circ$  yields 2.5 g. 3,6-dimethoxy-2-[2-hydroxy-5-methylbenzoyl]benzoic acid (II), m.  $218^\circ$ , and 2 g. 2,7-dimethyl-12,15-dimethoxyfluoran (III), m.  $290^\circ$ ; about 4 g. unchanged I is recovered. 2-Me ether (IV) of II, obtained

quant. with  $\text{Me}_2\text{SO}-\text{KOH}$ , m.  $203^\circ$ , is identical with the product obtained from **I** and  $p\text{-MeC}_6\text{H}_4\text{OMe}$  (cf. following abstr.). *1-Hydroxy-4-methyl-5,8-dimethoxyanthraquinone* (**V**) (1.5 g. from 2 g. **II** heated on the  $\text{H}_2\text{O}$  bath with concd.  $\text{H}_2\text{SO}_4$  and a pinch of  $\text{H}_3\text{BO}_3$ ), red, m.  $224^\circ$ , sol. in alkalis with red, in concd.  $\text{H}_2\text{SO}_4$  with blue to blue-red color and hydrolyzed by refluxing with const. boiling  $\text{HBr}-\text{AcOH}$  to the *1,5,8-tri-HO compd.* (**VI**), sol. in alkalis with blue-red, in  $\text{H}_2\text{SO}_4$  with blue to blue-red color. With *o*-cresol, 15 g. **I** gives 5 g. *3,6-dimethoxy-2-[2-hydroxy-3-methylbenzoyl]benzoic acid* (**VII**), m.  $191^\circ$ , and 18 g. *o*-cresol-3,6-dimethoxyphthalalein (*2,2-bis-[4-hydroxy-5-methylphenyl]-3,6-dimethoxyphthalide*) (**VIII**), m.  $258^\circ$ , changes from colorless to red at  $p_H$  9.1; the alk. absorption spectrum shows a peak at  $\lambda 580\mu$ . *2-Me ether* (**IX**) of **VII**, m.  $178^\circ$ , is not identical with the product obtained from **I** and *o*- $\text{MeC}_6\text{H}_4\text{OMe}$ . *Di-Me ether* (**X**) of **VIII**, m.  $202^\circ$ , is also formed in the condensation of **I** with *o*- $\text{MeC}_6\text{H}_4\text{OMe}$ . *1-Hydroxy-2-methyl-5,8-dimethoxyanthraquinone* (**XI**), red, m.  $165^\circ$ , sol. in alkalis with red, in  $\text{H}_2\text{SO}_4$  with blue to blue-red color. *1,5,8-Tri-HO compd.* (**XII**), red, sublimates  $250-60^\circ$ , sol. in alkalis with red, in  $\text{H}_2\text{SO}_4$  with blue-red color. *2,5,8-Trihydroxy-1-methylanthraquinone* (**XIV**) (1 g. from 3 g. **VIII** and 1.5 g. **I** in concd.  $\text{H}_2\text{SO}_4$  at  $125^\circ$ ), dark red, m.  $270^\circ$ , sol. in alkalis and  $\text{H}_2\text{SO}_4$  with bluish red color, is also obtained by condensing **I** with *o*- $\text{MeC}_6\text{H}_4\text{OMe}$ , dehydrating the product and demethylating the resulting anthraquinone. *3,6-Dimethoxy-2-[2-hydroxy-4-methylbenzoyl]benzoic acid* (**XV**), m.  $233^\circ$ , and *3-hydroxy-6-methoxy-2-[2-hydroxy-4-methylbenzoyl]benzoic acid* (**XVI**), crystals with  $\text{H}_2\text{O}$ , m.  $147^\circ$  and, anhyd.,  $187^\circ$ , are obtained in a combined yield of 15 g. from 20 g. **I** with *m*-cresol; at the same time is formed 17 g. *m*-cresol-3,6-dimethoxyphthalalein (*2,2-bis-[4-hydroxy-6-methylphenyl]-3,6-dimethoxyphthalalein*) (**XVII**), m.  $271^\circ$ , changes from colorless to red at  $p_H$  9.8; the alk. absorption shows a peak at  $\lambda 585\mu$ . *2-Me ether* (**XVIII**) of **XV**, from **XV** or **XVI** with alk.  $\text{Me}_2\text{SO}$ , m.  $189^\circ$ . *1-Hydroxy-3-methyl-5,8-dimethoxyanthraquinone* (**XIX**) (0.25 g. from 5 g. **XV**), red, m.  $172^\circ$ , sol. in alkalis with red, in  $\text{H}_2\text{SO}_4$  with blue-red color. *1,5,8-Tri-HO compd.* (**XX**), red, m.  $227^\circ$ , sol. in alkalis with blue, in  $\text{H}_2\text{SO}_4$  with blue-red color. The acid Ba salt of *3,5-(HO)\_2C\_6H\_3CO\_2H*, light yellow, was obtained in 2630 g. yield from 900 g.  $\text{BzOH}$ , 300 g.  $\text{P}_2\text{O}_5$  and 1500 cc. of 50% oleum at  $240-50^\circ$  and subsequent treatment with  $\text{BaCO}_3$ ; fused 8 hrs. at  $200-20^\circ$  with 1.5 parts of  $\text{KOH}$ , dissolved in  $\text{H}_2\text{O}$  and slowly treated, boiling hot, with  $\text{Me}_2\text{SO}$ , it gives 25-60% *3,5-(MeO)\_2C\_6H\_3CO\_2H*, whose Et ester  $b_p$   $199-200^\circ$ ; this with  $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  gives 93% *3,5-dimethoxytrichloromethylphthalide* which with  $\text{NaOH}$  at  $80-90^\circ$  yields 93% of dimethoxyphthalidicarboxylic acid; this, in turn, heated to  $180-5^\circ$ , gives 95% dimethoxyphthalide, which is quant. oxidized to *3,5,1,2-C\_6H\_2(OMe)\_2(CO\_2H)\_2*, whose anhydride (**XXI**) is also obtained quant. by refluxing with  $\text{Ac}_2\text{O}$ . *3,5-Dimethoxy-2-[2-hydroxy-4-methylbenzoyl]benzoic acid* (**XXII**) (14 g. from 20 g. **XXI**), m.  $233^\circ$ ; the phthalalein, simultaneously formed in 14 g. yield, could not be purified. *2-Me ether* (**XXIII**), m.  $219^\circ$ . *3,5-Dimethoxy-2-[4-methoxy-2-methylbenzoyl]benzoic acid* (**XXIV**), obtained in 40% yield from **XXI** and *m*- $\text{MeC}_6\text{H}_4\text{OMe}$ , m.  $233^\circ$ . Attempts to prep. a di-Me ether of emodin (**XXV**) by heating 5 g. **XXII** with 5 g.  $\text{H}_3\text{BO}_3$  and 7% oleum on the  $\text{H}_2\text{O}$  bath gave a very small amt. of a yellow substance, m.  $185^\circ$ , sol. in alkali like **XXIV** with red color and giving with alk.  $\text{Me}_2\text{SO}$  a yellow compd., m.  $175-80^\circ$ , which dissolved in concd.  $\text{H}_2\text{SO}_4$  with the same red color as trimethylemodin and whose absorption spectrum was very similar to that of the latter. *3,5-Dimethoxy-2-[2-hydroxy-4-methyl-5-nitrobenzoyl]benzoic acid*, obtained quant. from **XXII** in  $\text{AcOH}$  with  $\text{HNO}_3$  (d. 1.42) at  $50-60^\circ$ , light yellow, m.  $241^\circ$ . *3,5-Dimethoxy-2-[4-hydroxy-2-methyl-5-nitrobenzoyl]benzoic acid* (9 g. from 10 g. **XXI** with *3,4-Me(O\_2N)C\_6H\_3OH*), m.  $181^\circ$ . The above facts establish that in the condensation of the cresols with **I** the entering group takes the *o*-position to the HO of the cresols. The absorption spectra curves of the anthraquinones in slightly acid and alk. alc. solns. are given. All the curves of the anthraquinones having the quinizarin grouping (two  $\alpha\text{-HO}$  groups in the same ring) have the same general form, the acid being nearer the blue than the alk. band. The max. of the dimethoxymonohydroxy compds. are  $15-20\mu$  nearer the blue than those of the corresponding tri-HO compds. The bands in the *1,5,8-(HO)\_3* compds. shift toward the red as the Me moves from position 2 to 4 to 3. **II**, J. H. GARDNER with ROGER ADAMS. *Ibid* 2455-62.—Five g. **I** with *p*- $\text{MeC}_6\text{H}_4\text{OMe}$  and  $\text{AlCl}_3$  at  $70^\circ$  gives 3.5 g. *3,6-dimethoxy-2-[2-methoxy-5-methylbenzoyl]benzoic acid* (**XXVI**), m.  $203-4^\circ$ , and 2.2 g. *p*-cresol-3,6-dimethoxyphthalalein di-Me ether (*2,2-bis-[2-methoxy-5-methylphenyl]-3,6-dimethoxyphthalide*), m.  $187.5^\circ$ . Five g. **XXVI** heated rapidly to  $150^\circ$  with concd.  $\text{H}_2\text{SO}_4$  and poured upon ice gives 2.7 g. of a mixt. of *1,5,8-trihydroxy-4-methylantraquinone*, red, m.  $276-8^\circ$  (sublimation), sol. in  $\text{H}_2\text{SO}_4$  with blue-violet, in alkalis with violet-red color, and of the *1-hydroxy-5,8-dimethoxy compd.*, red needles with yellowish metallic gleam, m.  $224^\circ$ , sol. in  $\text{H}_2\text{SO}_4$  with blue-violet, in

NaOH with bluish red color; if the XXVI is heated 20 min. at 145–55° with the H<sub>2</sub>SO<sub>4</sub>, it gives 65% of the practically pure tri-HO compd. 3,6-Dimethoxy-2-[4-methoxy-5-methylbenzoyl]benzoic acid (XXVII) (1.9 g. from 5 g. I with *o*-MeC<sub>6</sub>H<sub>4</sub>OMe), m. 192°; at the same time is formed 8 g. *o*-cresol-3,6-dimethoxyphthalate di-Me ether (2,2-bis-[4-methoxy-5-methylphenyl]-3,6-dimethoxyphthalide) (XXVIII), m. 202–3°. 2-Methoxy-1-methyl-5,8-dihydroxyanthraquinone (2.5 g. from 5 g. XXVII heated rapidly to 150° with H<sub>2</sub>SO<sub>4</sub>), dark red, m. 249–9.5°, sol. in H<sub>2</sub>SO<sub>4</sub> with blue-violet, in alkalis with blue-red color 2,5,8-Tri-HO compd. (XXIX) (1.5 g. from 4 g. XXVII, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>3</sub> heated 30 min. at 150°), dark red, m. 270°, also obtained in 7.5 g. yield from 7 g. XXVIII and 3.5 g. I heated 2 days at 125° with concd. H<sub>2</sub>SO<sub>4</sub>. XXIX on distn. with Zn dust gives methylanthracene, which is oxidized to 1-methylanthraquinone, m. 167°. 3-Hydroxy-6-methoxy-2-[4-methoxy-1-methylbenzoyl]benzoic acid, m. 194.5°, is obtained in 85% yield from I and *m*-MeC<sub>6</sub>H<sub>4</sub>OMe. The facts above show that in the condensation of the cresol ethers the entering group takes the *p*-position to the MeO in the *o*- and *m*-ethers and the *o*-position in the *p*-ether. C. A. R.

**The synthesis of the methyl and ethyl esters of 1, 2, 3, 5-tetramethylpyrrole-4-monocarboxylic acid.** T. V. KORSHUN AND K. V. ROLL. *Bull. soc. chim.* 33, 1107–8 (1923).—AcCH<sub>2</sub>CO<sub>2</sub>Me was heated with MeCHClCO<sub>2</sub>Me and MeNH<sub>2</sub>, and the resulting product was steam distd. A small amt. of Me 1,2,3,5-tetramethylpyrrole-4-carboxylate, m. 101°, was obtained from the residue. The *Et* ester was prepd. by the action of MeNH<sub>2</sub> on *Et* diacetobutyrate, and was purified by crystn. from alc. followed by distn. under reduced pressure. A. C. PURDY

**Synthesis of some pyridylpyrroles.** J. P. WIBAUT AND ELISABETH DINGEMANSE. *Proc. Acad. Sci. Amsterdam* 26, 426–35 (1923).—Work is being carried out on a synthesis of an isomer of nicotine, in order to compare its physiol. properties with those of the natural isomer.  $\alpha$ -C<sub>6</sub>H<sub>4</sub>N NH<sub>2</sub> and mnic acid at 140° yield *N*-[ $\alpha$ -pyridyl]pyrrole (I), b<sub>760</sub> 260–1°, m. 17°. *Picrate*, m. 143°. *Methiodide*, yellow, m. 141.2°. A by-product of the above reaction appears to be  $\alpha,\alpha'$ -dipyridylamine (?), m. 95°. Upon distn. of I through a glass tube filled with pumice and heated to 670–90°, a mixt. of two *C*-pyridylpyrroles (II) is obtained, readily sepd. by steam distn. The II volatile with steam m. 90°; its solns. show a blue fluorescence. It does not give the pine chip reaction but gives a red-violet color with HCl and Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO. The K compd. (III) is an insol. yellow-brown powder. *Picrate*, yellow, m. 227–8°. *Methiodide*, yellow-brown, m. 148°. Oxidation of this isomer gave picolinic acid. The 2nd isomer, non-volatile with steam, m. 132.5°, is formed only in small amts. HCl and Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO give a cherry-red color changing to blue violet. The K compd. is a white powder. Oxidation likewise gives picolinic acid, indicating that the pyrrole nucleus in I is substituted at the  $\alpha$ -position, in the 2nd, the  $\beta$ -position. The action of MeI upon III in a sealed tube at 100° for 3 hrs. gave *C*-[ $\alpha$ -pyridyl]-*N*-methylpyrrole *methiodide*, yellow-brown, m. 186°. Slowly distd. with CaO, MeI is split off, giving the free pyrrole, the *picrate* of which m. 143°. This same deriv. appears to be formed in small amts. if the methylation is carried out at 50°. C. J. WEST

**Constitution of catechol.** I. JAMES J. DRUMM. *Proc. Roy. Irish Acad.* 36B, No. 5, 41–9 (1923).—This work was undertaken to det. if possible between the two types of formulas (chroman and coumaran) proposed for the catechols. Catechol tetra-Me ether (7 g.) in 50 cc. CS<sub>2</sub> reacts with 5 g. PCl<sub>5</sub> to give 6 g. of the *chloride* (I), m. 112°. Five g. I and 40–50 g. EtOH give 2.5 g. *Et* deriv., m. 123°; the concd. H<sub>2</sub>SO<sub>4</sub> soln. is yellow. PCl<sub>5</sub> has no action on the CS<sub>2</sub> soln. *Bu* deriv., m. 79–80°. Five g. I and 20 cc. C<sub>6</sub>H<sub>5</sub>N, heated to gentle boiling, give 4 g. *dehydrocatechol tetra-Me ether*, (II), m. 133.5–4.5°. It does not give a color with FeCl<sub>3</sub> while the concd. H<sub>2</sub>SO<sub>4</sub> soln. is a deep orange. The action of Br appeared to give a bright red monobromide, C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>Br, which, with EtOH and NH<sub>4</sub>OH, yields a color base, glistening needles, m. 133–4°. The *anhydrohydrochloride* of the color base, carmine-red, m. 126–8°, is quickly decolorized by EtOH; it is considered to be 5,7-dimethoxy-2-*m*,*p*-dimethoxyphenyl-1,4-benzopyranol *anhydrohydrochloride*. C. J. WEST

**Dioximes.** VII. G. PONZIO AND G. RUGGERI. *Gazz. chim. ital.* 53, 297–305 (1923); cf. C. A. 17, 2268.—The methylaminoglyoxime (I) described previously (C. A. 16, 2676) undergoes reactions by which it is connected with azoximes (furo-(ab)-diazoles) through previously unknown acyl derivs. and with methylaminofurazan (II), MeC<sub>2</sub>N<sub>2</sub>O.N<sub>2</sub>C<sub>2</sub>NH<sub>2</sub>, the 1st member of a new series of compds. I with excess

of Ac<sub>2</sub>O + anhyd. AcONa in the cold gave the *di-Ac* deriv. of I which, when dried thoroughly, m. 123°. This deriv. was boiled with excess Ac<sub>2</sub>O + NaOAc for some hrs.



The *Ac*-deriv. of 3-acetyl-5-methyl-(*ab*)<sub>1</sub>-diazole oxime,  $\text{AcNO}:\text{CMeC}:\text{N}:\text{O}:\text{CMe}:\text{N}$ ,

is formed; it is hydrolyzed on pouring the product into  $\text{H}_2\text{O}$ , giving 3-acetyl-5-methyl-furo-(*ab*)<sub>1</sub>-diazole oxime (III), m. 145°. III with  $\text{BzCl} + 20\%$  NaOH gives the *Bz* deriv., m. 198-9°. By heating I with 20% NaOH and  $\text{BzCl}$  3-acetyl-5-phenylfuro-(*ab*)<sub>1</sub>-diazole oxime (IV) is obtained as previously described (*l. c.*). With  $\text{BzCl} + \text{C}_6\text{H}_5\text{N}$  the *Bz* deriv. of IV is obtained, m. 174-5°. When III or IV is boiled with dil.  $\text{HCl}$   $\text{H}_2\text{O}$  is added and  $\text{AcOH}$  and  $\text{BzOH}$ , resp., split off, giving II, m. 72-3° (decompn.). II is also obtained directly from I by boiling with  $\text{Ac}_2\text{O} + \text{NaOAc}$ , pouring the product into  $\text{H}_2\text{O}$ , neutralizing with  $\text{Na}_2\text{CO}_3$  and extg. with  $\text{Et}_2\text{O}$ . The solvent is eliminated, the residue is boiled 0.5 hr. with 20%  $\text{HCl}$  and  $\text{HCl}$  and  $\text{AcOH}$  are eliminated by evapn. on the  $\text{H}_2\text{O}$  bath, after which II crystals out. With  $\text{Ac}_2\text{O} + \text{NaOAc}$  II gives the *mono-Ac* deriv., m. 115-6°; with  $\text{BzH}$  II gives the *benzylidene* deriv., m. 155-6°; with  $\text{PhCH}:\text{CH}:\text{CHO}$  II gives the *cinnamylidene* deriv., m. 126°. II in 30%  $\text{H}_2\text{SO}_4$  treated gradually with fine dry  $\text{KMnO}_4$  at 60-70° gives *azomethylfuran*, (V),  $(:\text{NC}:\text{N}:\text{O}:\text{N}:\text{CMe})_2$ ,

m. 107°. V hydrogenated with  $\text{PhNHNH}_2$  in  $\text{Et}_2\text{O}$  soln. gives *hydrazomethylfuran* (VI),  $(\text{NHC}:\text{N}:\text{O}:\text{ON}:\text{CMe})_2$ , m. 118-9° (decompn.). With  $\text{KMnO}_4$  as above VI

gives V. II in 20%  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  treated with  $\text{NaNO}_2$  seps. *azoinimomethylfuran*,  $\text{MeC}:\text{N}:\text{O}:\text{N}:\text{C}:\text{N}:\text{N}:\text{HNC}:\text{N}:\text{O}:\text{N}:\text{CMe}$ , m. 114°; the  $\text{EtOH}$  soln. with  $\text{AgNO}_3$

seps. the *Ag* salt; the *Ac* deriv.  $\text{Me}(\text{C}_2\text{N}_2\text{O})\text{N}:\text{NNAc}(\text{C}_2\text{N}_2\text{O})\text{Me}$ , m. 72°, was also obtained. VIII. G. PONZIO AND L. AVOGADRO. *Ibid* 305-11.—By the action of  $\text{PhNH}_2$  on the peroxide of  $\alpha$ -phenylglyoxime (phenylfuroxan) (I) in  $\text{C}_6\text{H}_6$ , Wieland and Semper (*C. A.* 2, 1012) obtained a compd., m. 180° (decompn.), which was considered to be  $\text{PhC}(\text{:NOH})\text{C}(\text{:NOH})\text{NHPh}$  (II) but was not studied further. Having previously found (*C. A.* 17, 2268) that phenylaminoglyoxime exists in 2 forms P. and A. were interested in detg. whether *phenylaminophenylglyoxime* (II) exists in 2 forms and found that it does. The  $\alpha$ -form (III) is best obtained by the reaction used by W. and S. by agitating powdered I with an equimol. amt. of  $\text{PhNH}_2$  in  $\text{H}_2\text{O}$  by which it is quant. transformed into pure III, which m. 187-8°, is sol. in NaOH or KOH and is reprecipitated with  $\text{AcOH}$ , is sol. unchanged in dil.  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  (but not in  $\text{HNO}_3$ ) and is reprecipitated with  $\text{NaOAc}$ . III when heated in  $\text{EtOH}:\text{H}_2\text{O}$  with dil.  $\text{AcOH}$  is isomerized slowly into the  $\beta$ -form (IV). III in boiling 20%  $\text{HCl}$  seps. the *HCl* salt, m. 208-9° (decompn.) on cooling. With  $\text{Ac}_2\text{O} + \text{NaOAc}$  III gives the *di-Ac* deriv. (V), m. 179°; in 20% NaOH it is slowly converted into III and some *phenylaminophenylfuran* (VI). The *di-Bz* deriv. of III, m. 201°, is dissolved unchanged in 20% NaOH. V boiled with 20% NaOH readily gives VI, m. 158°. IV is formed from III as stated but most readily by boiling  $\text{PhNH}_2$  and phenylchloroglyoxime in abs.  $\text{EtOH}$ . The mixt. is dild. with  $\text{H}_2\text{O}$ , acidified with  $\text{AcOH}$  and treated with 20%  $\text{Ni}(\text{OAc})_2$  by which the *Ni* salt,  $\text{Ni}(\text{C}_6\text{H}_5\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O}$ , m. 268° (decompn.), is pptd. This was heated with a small excess of 20%  $\text{HCl}$  from which the *HCl* salt of IV, m. 210-1° (decompn.) seps.; this with  $\text{NH}_4\text{OH}$  gave IV, m. 124° (decompn.). IV is sol. in NaOH and KOH and is pptd. unchanged with  $\text{CO}_2$  or dil.  $\text{AcOH}$ . The *di-Ac* deriv. of IV, m. 150°. *Methylaminophenylglyoxime* (VII) is formed thus:  $\text{MeC}(\text{:NOH})\text{C}(\text{:NOH})\text{Cl} + \text{PhNH}_2 \longrightarrow \text{MeC}(\text{:NOH})\text{C}(\text{:NOH})\text{NHPh} + \text{HCl}$  and from acetylphenylisouretine,  $\text{AcC}(\text{:NOH})\text{NHPh} + \text{NH}_4\text{OH}$ . When liberated from its *HCl* salt, VII decomps. rapidly. Only its *Ni* salt,  $\text{Ni}(\text{C}_6\text{H}_5\text{O}_2\text{N})_2$ , m. 242° (decompn.), is described; the *HCl* salt was isolated from this salt. IX. G. PONZIO AND L. AVOGADRO. *Ibid* 311-8.—In this paper new expts. on  $\alpha$ - and  $\beta$ -phenylglyoxime (I) and (II) are described, which demonstrate the great difference in behavior of the 2 forms and which constitute further confirmation of the opinion as to the inacceptability of the Hantzsch and Werner theory on the isomerism of the  $\alpha$ -dioxime. The behavior of I with concd.  $\text{H}_2\text{SO}_4$  and with  $\text{PhN}_2\text{Cl}$  is considered especially important. I heated briefly at 100° with concd.  $\text{H}_2\text{SO}_4$  gives phenylfuran, which is pptd. on diln. with  $\text{H}_2\text{O}$  and m. 35-6°. Under the same conditions but more slowly II gives 1-phenyl-3-oximinobenzyl-2-isoxazolone oxime, m. 218° (decompn.). When I in cold 10% NaOH is treated with a dil. soln. of  $\text{PhN}_2\text{Cl}$  a red-brown tar seps. This when purified gave  $\beta$ -benzyl dioxime (III), m. 207-8° (decompn.). III with  $\text{Ac}_2\text{O} + \text{NaOAc}$  gave the *di-Ac* deriv., m. 124-5°; the aq.- $\text{EtOH}$  soln. heated with dil.  $\text{AcOH}$  is slowly converted into diphenylglyoxime, m. 237°, identified as its *Ni* salt. When II is similarly treated with  $\text{PhN}_2\text{Cl}$   $\alpha$ -benzyl dioxime, m. 237-8° (decompn.), is obtained; with  $\text{Ni}(\text{OAc})_2$  it gives the characteristic *Ni* salt  $[\text{PhC}(\text{:NOH})\text{C}(\text{:NO-})\text{Ph}]_2\text{Ni}$ ; with  $\text{Ac}_2\text{O}$  it gives a *di-Ac* deriv., m. 150°. The distinctive properties of I and II in the above reactions

are discussed as confirming previous statements (C. A. 17, 2268) against the interpretation of the differences in I and II in terms of geometric isomerism (H. and W.).  $\text{Pr}_2\text{O}$  is not an energetic dehydrating agent and with I gives the *di-EtCO deriv.*, m. 75°; the *di-EtCO deriv.* of II, m. 80–90°. I cannot be benzoylated in NaOH or  $\text{C}_6\text{H}_5\text{N}$ . In  $\text{C}_6\text{H}_5\text{N}$  I gave the Bz deriv. of benzoyl cyanide oxime,  $\text{PhC}(\text{:NOBz})\text{CN}$ , m. 139–40°, which is easily explained by the fact that I is easily converted into phenylfurazan and this in turn into  $\text{PhC}(\text{:NOH})\text{CN}$ , m. 129°. II benzoylated in  $\text{C}_6\text{H}_5\text{N}$  gives the *di-Bz deriv.*  $\text{PhC}(\text{:NOBz})\text{C}(\text{:NOBz})\text{H}$ , m. 150°; it is sapon. in 20% NaOH, giving II.  $\text{BzCHBr}_2$  in EtOH with a slight excess of  $\text{NH}_2\text{OH} \cdot \text{HCl} + \text{NaOAc}$  heated some hrs. at 70–80° gave a mixt. of I and II which was sep. by a procedure previously described (C. A. 17, 2268). X. G. PONZIO AND L. AVOGADRO. *Ibid* 318–27.—In a previous paper (C. A. 17, 2268) P. and A. stated that in studying the nature of the isomerism of  $\alpha$ - and  $\beta$ -phenylaminoglyoxime (I) and (II)  $\text{N}_2\text{O}_4$  could not be used. The problem was solved by studying the action of  $\text{Ac}_2\text{O}$  on I and II.  $\text{Ac}_2\text{O}$  acting on I substitutes 2 H atoms, giving the *di-Ac deriv.*  $\text{PhC}(\text{:NOAc})\text{C}(\text{:NOH})\text{NHAc}$ , m. 150–1°; treated with 20% NaOH in the cold it gives the Ac deriv. of phenylaminofurazan (III), which is partly sapon. to III. The latter is the sole product if the mixt. is boiled. With  $\text{BzCl}$  I gives the *di-Bz deriv.* (IV),  $\text{PhC}(\text{:NOBz})\text{C}(\text{:NOBz})\text{NH}_2$ , m. 189–90° (decompn.), which with 20% NaOH IV is slowly converted into III and the oxime of 3-benzoyl-5-phenylfuro-(ab)-diazole (V),  $\text{PhC}(\text{:NOH})\text{C}(\text{C}_6\text{H}_5\text{O})\text{Ph}$ , m. 145°. II treated with  $\text{Ac}_2\text{O} + \text{NaOAc}$  gave the *di-Ac deriv.* (VI),  $\text{PhC}(\text{:NOAc})\text{C}(\text{:NOAc})\text{NH}_2$ , m. 133–4°. With 20% NaOH VI is partly sapon. to II and partly converted into the oxime of 3-benzoyl-5-methylfuro-(ab)-diazole (VII), m. 202–3° (decompn.). In melting VI is transformed into the Ac deriv. of III, m. 182–3°. The latter as well as VII with dil. HCl is sapon., giving III. VII in 10% NaOH with  $\text{BzCl}$  gives the Bz deriv.  $\text{PhC}(\text{:NOBz})\text{C}(\text{C}_6\text{H}_5\text{O})\text{Me}$ , m. 152–3°. II gives a *di-Bz deriv.*  $\text{PhC}(\text{:NOBz})\text{C}(\text{:NOBz})\text{NH}_2$ , m. 185–6°. This compd. with 20% NaOH gives II in part and some IV. The results summarized above further confirm P. and A.'s objections to the Hantzsch and Werner conception of the geometric isomerism of these compds. The results indicate that the 2 NOH groups in I are not equiv., while those in II are equiv. P. and A. have deduced the following rule: when a glyoxime  $\text{RC}(\text{:NOH})\text{C}(\text{:NOH})\text{R}'$  (where R' may be H or R) exists in 2 forms, one labile and the other stable (obtained from the labile form (called  $\alpha$ ), the 2 NOH groups behave toward reagents as if they have a different structure, while in the stable form (called  $\beta$ ) the 2 NOH groups have the same behavior toward all reagents. III was obtained in several ways as stated above but most conveniently quant. by boiling the *di-Ac deriv.* (VIII) of I a few mins. with NaOH; it m. 98–9°. VIII with NaOH in the cold gives the *mono-Ac deriv.* of III, m. 181–2°; this compd. is also obtained from VI on melting and from III with  $\text{Ac}_2\text{O}$  by heating for only a short time. III boiled with  $\text{Ac}_2\text{O} + \text{NaOAc}$  gives the *di-Ac deriv.* of III, m. 71°. III with  $\text{CrO}_3$  in boiling AcOH is dehydrogenated, giving azophenylfurazan (IX),  $\text{Ph}(\text{C}_6\text{H}_5\text{N}_2\text{O})\text{N}(\text{C}_6\text{H}_5\text{O})\text{Ph}$ , m. 134–5°. IX with  $\text{PhNHNH}_2$  in EtO gives hydrazophenylfurazan,  $[\text{Ph}(\text{C}_6\text{H}_5\text{O})\text{NH}]_2$ , m. 109°. When dehydrogenated it gives IX again. XI. G. PONZIO. *Ibid* 379–84.—P. has previously shown (C. A. 17, 2268) that it is only the  $\alpha$ -form (m. 168°) of phenylglyoxime (I) and not the  $\beta$ -form that reacts with  $\text{N}_2\text{O}_4$ , giving a compd.,  $\text{Ph}(\text{C}_6\text{H}_5\text{O}_2\text{H})_2$ , which Scholl (Ber. 23, 3504(1896)) considered to be phenylglyoxime peroxide (II),  $\text{PhC}(\text{:N} \cdot \text{O} \cdot \text{O} \cdot \text{N} \cdot \text{CH} \cdot \text{Wieland (C. A. 15, 2858)) found a labile isomer, m. 106–8°$ .

of II, having previously assigned  $\text{PhC}(\text{:N} \cdot \text{O} \cdot \text{N} \cdot \text{CH} \cdot \text{O}$  to II. Facts given in this paper

lead P. to conclude that there is but 1 form of II and that it is the oxide of benzoyl cyanide oxime (III),  $\text{PhC}(\text{:NOH})\text{C}(\text{:NO})$  (or  $\text{PhC}(\text{:NOH})\text{C}(\text{:N} \cdot \text{O})$ ). III on hydrolysis gives

$\text{NH}_2\text{OH}$ ,  $\text{BzOH}$  and  $\text{BzCN}$ ; treated with  $\text{Ac}_2\text{O}$  it gives the Ac deriv.,  $\text{PhC}(\text{:NOAc})\text{C}(\text{:N} \cdot \text{O})$ ,

m. 115–6°. Reduced with Zn dust + AcOH III gives benzoyl cyanide oxime, m. 129°, which was converted into the Bz deriv.,  $\text{PhC}(\text{:NOBz})\text{CN}$ , m. 139°, for identification. Formula III also permits of interpreting the reactions of II with  $\text{NH}_3$  (C. A. 2, 1012) and  $\text{PhNH}_2$  (P., l. c. above). P. concludes that I reacts in the tautomeric form  $\text{PhC}(\text{:NOH})\text{C}(\text{NO})\text{H}_2$  and is transformed by  $\text{N}_2\text{O}_4$  into  $\text{PhC}(\text{:NOH})\text{C}(\text{NO})\text{NO}_2\text{H}$  which, being unstable, loses  $\text{HNO}_2$ , giving III. II is readily obtained from I by the method previously described (l. c.) and seps. as white crystals that soften at 105° and m. 108°. On recrystn. from org. solvents it m. 102°, but if the crystals are dissolved in EtO and treated with a little  $\text{N}_2\text{O}_4$ , they again sep. having the m. p. 108°. It may be

preserved unchanged in Pt but yellows with decompn. in contact with glass (due probably to its sensitiveness to alkali). A specimen 2 years old with a lower m. p. was restored to its original m. p. by the above process. XII. G. PONZIO. *Ibid* 507-13. Formula III for the compd. II in the above abstract does not conform with the alleged isomerization of II into phenylhydroxyfufuran,  $\text{PhC:N.O.N:COH}$ , which

Wieland and Semper (*Ann.* 358, 36(1906)) state is brought about by alkali hydroxides and carbonates. P. has found that the alleged isomer is merely less pure III than W. and S. obtained in their 1st expts. The additional reactions of II described in this paper can be interpreted best by formula III. When compd. II is boiled for an hr. with xylene or treated at room temp. in  $\text{C}_6\text{H}_6$  with  $\text{PhNHNH}_2$ , the 3-phenyl-5-hydroxyfuro-(ab)-diazole (IV) of Tiemann and Falck (*Ber.* 1482(1886)), m. 202-3°, is formed. IV with the calcd. amt. of  $\text{Na}_2\text{CO}_3$  gives the Na salt  $\text{Ph(C}_6\text{H}_4\text{N}_2\text{O)ONa}$ . With  $\text{Me}_2\text{SO}$ , IV gives the Me ether,  $\text{Ph(C}_6\text{H}_4\text{N}_2\text{O)OMe}$ , m. 116°. W. and S. state that Grignard's reagent does not react with II but P. found that  $\text{MgIme}$  reacts easily in  $\text{Et}_2\text{O}$  soln., sepg. an addn. product which, treated with  $\text{HCl}$ , gives phenylmethylglyoxime (which was sepd. as the Ni salt (*C. A.* 16, 908)). The expts. of W. and S. on the action of  $\text{Na}_2\text{CO}_3$  on II were repeated. P. proved that the product is not phenylhydroxyfufuran as stated by them but an impure III, as was proved by purifying it in  $\text{Et}_2\text{O}$  + a little  $\text{N}_2\text{O}_4$  (cf. preceding abstr.).

E. J. WITZEMANN

**Preparation and properties of 1-mercaptobenzothiazole, its homologs and derivatives.** L. B. SEBERELL AND C. E. BOORD. *J. Am. Chem. Soc.* 45, 2390-9(1923).—1-Mercaptobenzothiazole (I) and its derivs. were prepd. in 4 ways: by heating S 1-2 hrs. at 225-50° in an autoclave with (1) the appropriate disubstituted thiourea, (2) the Zn aryldithiocarbamate, (3) the  $\text{NH}_4$  salt of the same acid, and (4) a mixt. of the arylamine and  $\text{CS}_2$ . In the prepn. of I by method (1) is formed an alkali-insol. residue of 1-anilidobenzothiazole (II), which is hardly produced at all in (3) and (4); the insol. residue obtained in (2) consists almost entirely of  $\text{ZnS}$ . The formation of I and II is explained by assuming that the  $\text{CS(NHPh)}_2$  is in equl. with its tautomeric form which occurs in the 2 geometrical isomers  $\text{PhNHCSH}$  and  $\text{PhNHCSSH}$ ; sulfurization of the



former and subsequent elimination of  $\text{H}_2\text{S}$  would give II while sulfurization of the 2nd isomer and elimination of  $\text{PhNH}_2$  would give I; the combined yield of I and II accounts for 90-6% of the  $\text{CS(NHPh)}_2$  used. S. and B. believe that the mercaptobenzothiazoles are similarly formed from the aryldithiocarbamates by direct sulfurization and subsequent elimination of a hydrosulfide. Method (3) in general gives the best yields but the products obtained by (2) contain less tarry material and are more readily purified. The more highly substituted the arylamine, the lower is the yield of thiazole. The mercaptobenzothiazoles are oxidized in alc. or alkali by alc. I to the corresponding disulfides; the Zn salts of the thiazoles are prepd. by pptn. from solns. of the  $\text{NH}_4$  salts with  $(\text{NH}_4)_2\text{ZnO}_2$  or from alc. solns. of the free thiazoles with aq. solns. of any Zn salt; the normal Pb salts are obtained from the free thiazoles in alc. or their Na salts in  $\text{H}_2\text{O}$  with aq. solns. of Pb salts, the basic Pb salts from alk. solns. of the thiazoles with  $\text{Pb(OH)}_2$  in an excess of  $\text{NaOH}$ . II, obtained in 16.5% yield in the prepn. of I by method (1), light yellow, m. 154°. I, obtained in 73.3% yield, light yellow, m. 177°; disulfide, amorphous, slightly yellow, m. 176° (yield, 87%); Zn, normal Pb (bright yellow) and basic Pb salts, amorphous. 3-Me deriv. of I, m. 186°; disulfide, m. 162°; Zn, normal (bright yellow) and basic Pb salts. 4-Me isomer, light yellow, m. 163°; disulfide, m. 195°. 5-Me isomer, very light yellow, m. 181°; disulfide, m. 201-2°; Zn salt. 3,5-Di-Me deriv. of I, light yellow, m. 250.5°; disulfide, m. 193°. 5-EtO deriv. of I, cream-colored, m. 198°. 5-MeO compd., light yellow, m. 201°.

C. A. R.

**Action of benzenesulfone azide upon malonic ester.** THEODOR CURTIUS AND GUSTAV EHRHART. *J. prakt. Chem.* 106, 66-76(1923).— $\text{PhCH}_2\text{N}_3$  reacts with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  to form  $\text{PhCH}_2\text{NHCH}(\text{CO}_2\text{Et})_2$ . It might be expected that  $\text{PhSO}_2\text{N}_3$  would react similarly and give  $\text{PhSO}_2\text{NHCH}(\text{CO}_2\text{Et})_2$ , which upon hydrolysis should give  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ , thus leading to a simple synthesis of  $\text{NH}_2$  acids. When, however, 4.5 g.  $\text{PhSO}_2\text{N}_3$  and 8 g.  $\text{CH}_2(\text{CO}_2\text{Et})_2$  are boiled for 5 hrs. at 100° (20-25 mm.) no gas evolution occurs and the reaction product, extd. with 1:10  $\text{NaOH}$  and acidified with dil.  $\text{H}_2\text{SO}_4$ , yields 1-benzenesulfone-4-carboxylic acid-5-hydroxytriazole, thick yellow oil, which gradually solidifies, forming 1-benzenesulfone-4-carboxylic acid-5-triazolone (benzenesulfaminodiazomalononic acid) (I) (yield, 2.5 g.), anisotropic crystals, m. 106° (decompn.). The Et ester (II), m. 79°, results by treating the above reaction product with the calcd. amt. of  $\text{EtONa}$ . It is sapond. by dil. aq.  $\text{NaOH}$  and at 100° loses N. II, heated with

5 parts concd.  $\text{NH}_4\text{OH}$  in a tube several hrs. at  $70^\circ$ , yields the acid amide, decomps. without m. Heated in  $\text{EtOH}$  with 3 mols. of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  II gives the *bis-NH<sub>2</sub>* salt of 1-amino-4-benzenesulfaminocarboxylic acid-5-hydroxy-1,2,3-triazole, small anisotropic tables, which, with  $\text{HCl}$ , yields the free acid, small prisms, the benzal compd. of which forms needle-like prisms, and is decompd. by hot, rather concd.  $\text{H}_2\text{SO}_4$ . Attempts to split off N from the triazole form of I, using the Na salt, showed that upon heating the reaction proceeds with explosive violence at a definite point. C. J. WEST

**Derivatives of 2-aminopyridine, 2-aminoquinoline and 4-aminoquinoline.** E. DIPOLDER. *J. prakt. Chem.* 106, 41-6 (1923).—A general introduction to work reported here and to be reported later. Action of 2-chloropyridine upon *o*-aminophenol. With E. DIUERLEIN. *Ibid* 46-52.— $\text{o-H}_2\text{NC}_6\text{H}_4\text{OH}$  and 2  $\text{ClC}_5\text{H}_4\text{N}$  give a yellow and a white reaction product (C. A. 17, 3261). The former is *o*-hydroxyphenylimino-1,2-dihydropyridine (I), of which the following derivs. are described: *HCl* salt, sinters  $148^\circ$ , m.  $153-4^\circ$ . Picrate, yellow, sinters  $162^\circ$ , m.  $172-3^\circ$ . Chloroplatinate, dark yellow, m.  $180^\circ$  (decompn.).  $\text{HgCl}_2$  salt of the *HCl* salt, sinters  $134^\circ$ , m.  $149-151^\circ$ .  $\text{HgCl}_2$  salt of the base, m.  $180-2^\circ$ . Nitrosamine, yellow-brown, m.  $275-6^\circ$  (decompn.). Methiodide, yellow-brown, m.  $188-91^\circ$  (decompn.).  $\text{NaOH}$  gives a dark yellow soln. from which  $\text{CO}_2$  ppts. a yellow compd.,  $\text{C}_{12}\text{H}_{17}\text{ON}_2$ , m.  $116-7^\circ$ ;  $\text{HI}$  regenerates the methiodide. The colorless product accompanying I is *o*-hydroxyphenyldipyriddyamine, m.  $187^\circ$ , prepd. by heating 2 mols. 2- $\text{ClC}_5\text{H}_4\text{N}$  and 1 mol.  $\text{o-H}_2\text{NC}_6\text{H}_4\text{OH}$  in a tube at  $200^\circ$ , or in varying yields by heating the components with  $\text{BaO}$ . *HCl* salt, sinters  $132^\circ$ , m.  $242-4^\circ$ . Chloroplatinate, pale orange-yellow, m.  $212-5^\circ$  (decompn.). Chloraurate, orange, m.  $195^\circ$ . Picrate, yellow, m.  $190^\circ$ .  $\text{HgCl}_2$  salt of base, sinters  $155^\circ$ , m.  $169-72^\circ$ .  $\text{HgCl}_2$  salt of the *HCl* salt, m.  $206-8^\circ$ . Dipyriddy-, diquinolyl-, and pyridylquinolylamines. *Ibid* 53-65. Dipyriddyamine (C. A. 17, 3261) is conveniently isolated by concg. the steam distillate, after adding  $\text{HCl}$ , and liberating the base with  $\text{NH}_3$ .  $\text{HgCl}_2 \cdot \text{HCl}$  salt,  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Hg}$ , sinters  $113^\circ$ , m.  $225^\circ$ . Methiodide, yellow, m.  $288-91^\circ$ . 2-Aminoquinoline is readily prepd. by heating the *Cl* deriv. with 5 parts  $\text{ZnCl}_2 \cdot \text{NH}_4\text{OH}$  and some  $\text{NH}_4\text{Cl}$  in a tube at  $210^\circ$  for 8 hrs. Above  $220^\circ$  considerable amts. of carbostyryl is obtained. Heating the 2- $\text{Cl}$  and 2- $\text{NH}_2$  derivs. with  $\text{BaO}$  8 hrs. at  $200-210^\circ$  gives diquinolylamine, pale yellow, m.  $161^\circ$ . *HCl* salt, does not m.  $305^\circ$ .  $\text{AuCl}_3$  salt, orange-yellow, sinters  $261^\circ$ , m.  $306^\circ$ .  $\text{HgCl}_2$  salt, pale yellow, m.  $272^\circ$ . Monopicrate, yellow, m.  $286^\circ$  (decompn.). Dipicrate, yellow, m.  $297^\circ$  (decompn.). Nitrosamine, pale yellow, m.  $238^\circ$  (decompn.). Methiodide, yellow, sinters  $246^\circ$ , m.  $278^\circ$ . 4,4-Dimethyldiquinolylamine, canary-yellow, m.  $167.5^\circ$ . *HCl* salt, pale yellow, m.  $292-7^\circ$ .  $\text{HgCl}_2$  salt, m.  $249^\circ$ . Chloroplatinate, pale yellow, m.  $280^\circ$  (decompn.). Monopicrate, yellow, decomp.  $286-299^\circ$ . Dipicrate, dark yellow, darkens  $265^\circ$ , decomp.  $289^\circ$ . Nitrosamine: pale yellow, decomp.  $238^\circ$ . Methiodide, yellow, darkens  $245^\circ$ , m.  $290^\circ$ . Pyridylquinolylamine, pale yellow, m.  $108^\circ$ . *HCl* salt, yellow, decomp.  $215-6^\circ$ . Monopicrate, darkens  $223^\circ$ , m.  $242-4^\circ$ .  $\text{HgCl}_2$  salt of base, pale yellow, m.  $210^\circ$ .  $\text{HgCl}_2 \cdot \text{HCl}$  salt, pale yellow, m.  $245^\circ$ . Methiodide, light yellow, m.  $208^\circ$ . Pyridyl-4-methylquinolylamine, pale yellow, sinters  $158^\circ$ , m.  $174^\circ$ . *HCl* salt, darkens  $190^\circ$ , m.  $241^\circ$ . Methiodide, bright yellow, m.  $208^\circ$ . 4-Methyldiquinolylamine, yellow, m.  $129^\circ$ . *HCl* salt, pale yellow, m.  $275^\circ$  (decompn.). Monopicrate, yellow, sinters  $279^\circ$ , decomp.  $287^\circ$ . Methiodide, yellow, darkens  $217^\circ$ , m.  $247-53^\circ$  (decompn.). C. J. WEST

**Strychnine.** I. E. OLIVERI-MANDALA and G. COMELLA. *Gazz. chim. ital.* 53, 276-84 (1923).—The gradual degradation of strychnine (I),  $\text{C}_{21}\text{H}_{27}\text{O}_2\text{N}_2$ , with oxidizing agents, although often attempted in the last 50 years, has not given satisfactory results as with other even more complex alkaloids. O. M. and C. proposed to oxidize a  $\text{H}_2\text{O}$ -sol. deriv. of I and finally selected hydroxystrychnine (II). On treatment with  $\text{KMnO}_4$ , however, II gave an acid deriv. of indole which could not be purified. Dehydrogenation of I in the presence of Ni gave degradation products of little or no value in the solution of the problem of the constitution of I. Perkin and Robinson (C. A. 4, 1613) assigned a structure to I in which a  $\text{CHOH}$  group forms a part of a hydrogenated aromatic ring. This ring on oxidation should first give a cyclohexanone and then by ring rupture and further oxidation a bi- $\text{CO}_2\text{H}$  deriv. This same ring on dehydrogenation should give a phenolic  $\text{OH}$  deriv. Attempts to realize these reactions failed so that O. M. and C. conclude that the behavior of I is not in accord with the existence of an easily oxidizable  $\text{CHOH}$  group in it. Moreover, the optical rotation of I should be destroyed by oxidation of  $\text{CHOH}$  to  $\text{CO}$  if the formula of C. and R. is correct, whereas strychninonic acid and other derivs. contg. the  $\text{CO}$  group (Leuchs, Ritter, C. A. 14, 1329) retain their optical activity. After a review of the facts on the isomerization of I it is concluded that the  $\text{C}(\text{OH})\text{Me}$  group can explain some of the transformations of strychnine. 10 g. II in 300 cc.  $\text{H}_2\text{O}$  were treated at room temp. with 5%  $\text{KMnO}_4$  until it was no

longer decolorized. This gave an acid (III),  $C_{12}H_{10}O_4N_2 \cdot 2H_2O$ , m.  $280^\circ$  (decompn.), identical with that obtained by Leuchs (*C. A.* 2, 2387) by oxidizing I in  $Me_2CO$  with  $KMnO_4$ . As the temp. of oxidation is increased the amt. of III formed is diminished and an indole deriv. is obtained in increasing amts. This product was subjected to dry distn. with  $CaO$  and gave indole as the picrate. This proves that I undoubtedly contains an indole complex. This preliminary report is to be continued. E. J. W.

**Preparation of dicyanodiamide from calcium cyanamide.** H. C. HETHERINGTON AND J. M. BRAHAM. *Ind. Eng. Chem.* 15, 1060-3 (1923).—The purpose of the work was to find data upon which to base large-scale production of dicyanodiamide (I). The difficulty in treating  $CaCN_2$  with  $H_2O$  is that  $H_2CN_2$  does not polymerize to I in good yields, the acid salt,  $Ca(HCN_2)_2$ , being unstable in soln. Products other than I are melamine, cyanourea and  $NH_4$ . The crux of the process is in converting  $Ca(HCN_2)_2$  successfully. References to work on the reaction are given. The Grube and Kruger process (Ger. pat. 279,133, *C. A.* 9, 1087) showed most promise; the essential feature is that the concn. of  $HCN_2^-$  and undissociated  $H_2CN_2$  be as 1:1. The procedure for the extn. of  $CaCN_2$  is given and the data obtained are tabulated. Methods of establishing the 1:1 ratio are given. The effect of temp. on the transformation of cyanamide was studied. The soly. of I in  $H_2O$ , alc. and  $Et_2O$  was detd. At  $0^\circ$ , 100 g.  $H_2O$  contain 1.27 g. I, and the values for 7 other temps. are given. In 100 g. alc. 0.937 g. I are dissolved and in  $Et_2O$ , 0.0006 g. H. E. WILLIAMS

**Oxidation of carbohydrates.** JULIUS STIEGLITZ. *Proc. Inst. Medicine of Chicago* 1, 41-50 (1916-17).—The oxidation of glucose is an intra-atomic phenomenon involving the loss of electrons by the C atoms of glucose and is essentially of the same character as is the oxidation of a simple element like H or Zn. The production of an elec. current was anticipated from this point of view and realized. The oxidation of glucose is enormously accelerated by the presence of alkalies and it is retarded by the presence of neutralizing acids. The alkali acts by shifting the equil. conditions of glucose so as to give a much larger concn. of the oxidizable component, by exposing the negative charge of the C atoms involved. The important increase in potential in the course of time shows that the decompn. products resulting from the action of alkali and oxidation on glucose, or of alkali alone, are much more oxidizable even than glucose itself. The fact that such sugars as are not directly oxidizable in the body give the same order of high potentials, when investigated in this way, shows that there is some fundamental sp. factor, probably the oxidizing enzymes, whose influence in the body is of paramount importance in the physiology of the oxidation of carbohydrates. C. J. WEST

**Double bond of some ethylene derivatives of camphor obtained by catalytic hydrogenation.** J. DÉTRIE. *Bull. soc. chim.* 33, 1263-84 (1923).—See *C. A.* 17, 1223.

E. J. C.

**Asteriasterol (PAGE) 111.** Influence of ultra-violet radiation in the presence and absence of catalyzers on the reactivity of a halogen bound to the C ring (ROSENMUND, *et al.*) 3. X-ray investigation of fatty acids (MÜLLER) 3. Manufacture of chemicals by electrolysis (III) organic compounds (CLARKE) 4. Crystalline structure of anhydrous racemic acid (ASTBURY) 2.

**Anthraquinone.** A. ULLRICH. U. S. 1,466,683, Sept. 4.  $C_{14}H_{10}$  is heated at about  $90^\circ$  with stirring in a closed vessel with 5 times its wt. of anhydrous  $HOAc$  and 0.6 its wt. of  $Ac_2O$ . A small amt. of  $NaNO_2$  is added and O is introduced under pressure. Oxidation takes place with formation of anthraquinone. When the oxidation is finished after several hrs. the anthraquinone is filtered and washed with glacial  $HOAc$ . A 95% yield is obtained. The process may also be carried out by using O carriers such as  $MnO_2$  or  $BaO_2$  and  $H_2O$ -fixing reagents such as  $Na_2SO_4$ , anhydrous  $NaOAc$ , propionic anhydride or phthalic anhydride. Oxanthranol, monochloroanthracene, dichloroanthracene and similar compds. also may be oxidized in the same manner.

**Anthraquinone.** A. ULLRICH. U. S. 1,467,258, Sept. 4.  $C_{14}H_{10}$  or its derivs. are oxidized by a process similar to that of U. S. 1,466,683 (preceding abstract) except that  $H_2O$  may be present in the reaction mixt., e. g., ordinary concd.  $HOAc$  may be used instead of anhydrous  $HOAc$  or metal salts of org. acids may be used in aq. soln. as well as in dry form.

**Hydrazoanisole.** R. A. NELSON. U. S. 1,469,586, Oct. 2. *o*-Nitroanisole is reduced with Zn and caustic alkali in the presence of alc. at boiling temp. and the reduction mass is slowly cooled while shaking or agitating to permit the growth of hydrazoanisole crystals. The product is mixed with  $H_2O$  and the crystals are sepd. from the Zn residue by sieving.

**Quinizarin.** D. SEGALLER and D. H. PRACOCK. U. S. 1,465,689, Aug. 21. Quinizarin is prepd. by heating a mixt. of phthalic anhydride, PhOH,  $H_2BO_3$  and  $H_2SO_4$  in three successive stages of 3 hrs. each at 180°, 200° and 238–40°, pouring the reaction mixt. on ice and sepg. the quinizarin by filtering off and washing with cold  $H_2O$ , pressing, stirring to a paste with  $H_2O$ , boiling for a few min., filtering hot, washing with boiling  $H_2O$  and drying.

**Dihydrooxycodone.** M. FREUND. U. S. 1,468,805, Sept. 25. Dihydrooxycodone, m. 222°, is obtained by reducing oxycodone in an HOAc soln. by mol. H in the presence of a metal catalyst such as Pt black.

**2,3-Hydroxynaphthoic acid.** R. N. WALLACH. U. S. 1,470,039, Oct. 9. Anhyd. Na  $\beta$ -naphtholate is dissolved in  $\beta$ -naphthol and the resulting soln. subjected to the action of  $CO_2$  at a temp. of 200–300° under a pressure of over 200 lbs. per sq. in.

**Terpene phenols.** H. WUYTS. U. S. 1,469,709, Oct. 2. Equimol. proportions of carvene and PhOH are caused to react in the presence of  $\beta$ -toluenesulfonic acid, the temp. being maintained below 105°. The reaction product is treated with steam and subsequently treated with KOH or NaOH in the presence of toluene or equiv. solvent at a temp. of about 70–80° and sepd. into 2 layers, the alk. soln. from which yields terpene phenols on solidification, which may be used as *antiseptics* or for the manuf. of *varnishes* or *insulators*.

**Hydrocarbons: halogen hydrocarbons.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Brit. 196,272, April 5, 1923. Halogen-substituted hydrocarbons or mixts. thereof are converted with elimination of HCl into hydrocarbons or other halogen-substituted hydrocarbons contg. a higher no. of C atoms by conducting them, in admixt. with  $H_2O$ , over certain catalysts at a raised temp. not exceeding 400°. The catalysts comprise metals, certain non-metals, and metallic compds., such as  $ThO_2$ ,  $ZrCl_4$ ,  $Bi_2O_3$ ,  $SnCl_4$  and  $ZnCl_2$ , and are mounted on porous materials, particularly highly active charcoal. Pressures higher than atm. may be employed. Examples are given.

**Chlorinating hydrocarbons.** C. P. TOWNSEND. U. S. 1,468,220, Sept. 18. Chlorination of hydrocarbons, e. g.,  $C_4H_8$  to form  $C_4H_7Cl$ , is effected by leading the reaction products including hydrocarbon in vapor form together with Cl and HCl into a body of  $H_2O$  in which  $MnO_2$ , ZnO or other reactive metal oxide is suspended. This serves to effect sepn. of liquid hydrocarbon and causes further chlorination.

**Hydrogenating benzene.** T. MIDGLEY, JR. U. S. 1,467,905, Sept. 11. H and  $C_6H_6$  vapor are introduced continuously under pressure into a catalytic mass.

**Ethyl alcohol; ammonium sulfate.** COMPAGNIE DE BÉTHUNE. Brit. 197,315, April 17, 1923. EtOH is obtained from  $EtHSO_4$  by treatment with a reagent which fixes the  $H_2SO_4$  content with evolution of heat, thereby causing the distn. of the alc. without the application of external heat.  $NH_3$ , either as gas or in the form of a soln., is described as the reagent, in which case  $(NH_4)_2SO_4$  is obtained as a by-product. According to the example, a stream of  $NH_3$  gas is conducted into  $EtHSO_4$  or  $H_2SO_4$  contg.  $EtHSO_4$ ; the alc. distills off to a dephlegmator and is condensed;  $(NH_4)_2SO_4$  settles out or remains dissolved in the  $NH_3$ -satn. vessel. The operation may be carried out at normal or reduced pressure.

**Benzaldehyde; benzoic acid.** CARBIDE & CARBON CHEMICALS CORPORATION. Brit. 197,319, April 24, 1923. BzH and benzoic acid are obtained by bringing free O into contact with dibenzyl at elevated temps. The dibenzyl may be employed in the liquid or vapor phase; O or O-contg. gases, such as air, may be used; and the oxidation may take place at normal or increased pressure. A suitable construction is specified.

**Formic acid.** H. NIELSON and B. LAING. Brit. 198,385, Dec. 3, 1921. Comprises (1) the production of formic acid by the oxidation of  $CH_4$  with a metallic oxide or by the interaction of CO and water vapor in the presence of a catalyst, preferably a metallic oxide; and (2) the destructive distn. of carbonaceous material in the presence of formic acid vapor for the purpose of increasing the yield of condensible hydrocarbons. In (1)  $CH_4$  or a mixt. of CO and water vapor is passed at a temp. of 250° to 800° over a metallic oxide, which preferably comprises an "activated Cu suboxide," prepd. either by pptg. Cu from a soln. of  $CuSO_4$  with metallic Zn, and then washing, drying and roasting the ppt. in air, or by moistening other Cu ppts. from Cu salts or granulated or powd. Cu with dil.  $ZnSO_4$  soln., followed by washing, drying and heating in air. After a short time the Cu suboxide becomes inactive and must be reactivated by moistening with dil.  $ZnSO_4$  soln., washing, drying, and roasting in air. Gases such as air gas, water gas, coal gas or natural gas may provide the source of the  $CH_4$  or CO; and their sensible heat, if any, may be utilized for the formic acid reaction, which is endothermic. In the destructive distn. of carbonaceous materials, which may comprise coal, lignite, peat, shale, wood, or liquid hydrocarbons, the formic acid, which may be prepd. as described

above, is introduced in the vapor phase into the distn. vessel. The carbonaceous material may contain a small % of admixed carbonates of Na, K or Ca; and the distn. vessel may be heated internally by the sensible heat of the whole or a part of the air gas or water gas before conversion into formic acid. It is stated that hydrocarbon gases may be similarly treated; thus,  $C_2H_2$  may be converted into HOAc.

**Methane.** T. P. BIRCHDEN & J. CROSFIELD & SONS LTD. Brit. 198,023, Dec. 14, 1921. Com. water gas, contg. approx. equal proportions of CO and H<sub>2</sub>, is passed over a catalyst maintained at a temp. of 220-300° and preferably not higher than 280°. The reaction takes place according to the equation:  $-2CO + 2H_2 = CO_2 + CH_4$ . The catalyst is Ni or Co or a mixt. thereof and is preferably mounted on a carrier. The process may be applied to the methane enrichment of water gas or to the production of pure CH<sub>4</sub>. In the latter case, CO<sub>2</sub> is first eliminated and then residual traces of CO and H are removed by passage over heated CuO at a temp. of 200° to 250°, the CH<sub>4</sub> being finally sepd. from N by liquefaction.

**Quinoline derivatives; dyes.** J. A. GARDNER and M. WILLIAMS. Brit. 198,462, March 13, 1922. In the synthesis of quinoline and its derivs. by the Skraup reaction or the Döbner and von Miller reaction chloropicrin is employed as the oxidizing agent. In examples the use of chloropicrin in the production of the following compds. is described: quinoline, 6- or 8-methylquinoline, 5,8-dimethylquinoline and 8-hydroxyquinoline, from glycerol and the corresponding aromatic amine; alizarin blue from  $\beta$ -aminoanthraquinone and glycerol; 2-methylquinoline from aniline and paraldehyde.

**Chlorohydrins.** B. E. ELDRED and B. T. BROOKS. U. S. 1,465,601, Aug. 21. A mixed soln. of HOCl and Na borate is used for treating gaseous unsatd. hydrocarbons such as gaseous olefine mixts. to form chlorohydrins, sol. chloride and H<sub>3</sub>BO<sub>3</sub>; the latter is removed from the soln. by chilling and the chlorhydrin is recovered by distn. or extrn. An app. is described for carrying on this process, Cl gas being supplied to the soln. to form the HOCl. Cf. C. A. 17, 2428.

**Chlorohydrins.** B. T. BROOKS. U. S. 1,465,595, Aug. 21. See Can., 221,754 (C. A. 16, 3316).

**Separating olefins from gaseous mixtures.** B. E. ELDRED. U. S. 1,465,600, Aug. 21. A gaseous mixt. contg. propylene, ethylene and satd. hydrocarbons is treated to obtain a concn. of the propylene by subjection under pressure to the action of an absorbent such as "gas naphtha" which will selectively absorb the propylene followed by distn. of the propylene from the absorbent.

**Purifying acetic anhydride.** C. J. STROSACKER and C. C. SCHWÄGLER. U. S. 1,467,074, Sept. 4. Ac<sub>2</sub>O contg. a S compd. such as thioanhydride having substantially the same b. p. as the Ac<sub>2</sub>O as an impurity is treated with a Mn oxide or other metal oxide (which although insol. in the material will unite with the S compd.) and the Ac<sub>2</sub>O is then distd.

**Phenyglycine compounds.** M. WYLER. U. S. 1,467,598, Sept. 11. One mol. proportion of C<sub>6</sub>HCl<sub>3</sub> is pumped into a mixt. contg. a very slight quantity in excess of one mol. proportion of PhNH<sub>2</sub> and CaO or other equiv. compd. of alk. reaction, under pressure, at a temp. of 170-180°, in order to obtain a salt of phenyglycine.

**Polymerizing glycerol.** R. I. BASHFORD. U. S. 1,467,299, Sept. 11. A metallic chloride, e. g., ZnCl<sub>2</sub>, is used for polymerizing glycerol at a temp. of 220-60°.

**Refining camphor.** R. L. ANDREAU. U. S. 1,468,371, Sept. 18. Crude camphor which may contain terpenes of high and low b. p. or two substances of similarly different boiling points is heated to vaporize the constituent of lower b. p. and the entrained constituent of higher b. p. is collected in a series of liquid layers in a rectifying column or similar device the liquid layers of which are supplied with heat additional to that carried by the vapors themselves to facilitate fractionation. Condensate is refluxed and the vapor of material of lower b. p. is separately condensed.

**Purifying camphor.** J. E. CRANE and E. G. LOOMIS. U. S. 1,468,377, Sept. 18. Crude camphor is heated to a vaporizing temp. and the temp. is maintained sufficiently long to decompose org. impurities which are present in the camphor; the camphor fumes are scrubbed through liquid camphor and condensed while continuously removing the condensate.

**Metalddehyde.** E. LÜSCHER and T. LICHTENHÄHN. U. S. 1,467,733, Sept. 11. In the manuf. of metalddehyde from acetaldehyde a small amt. of CaBr<sub>2</sub> is employed as a catalyst together with a small amt. of HCl.

**Phenol.** P. COTTRINGER. U. S. 1,466,991, Sept. 4. In the production of PhOH from C<sub>6</sub>H<sub>6</sub> or in similar processes, a phenate, e. g., C<sub>6</sub>H<sub>5</sub>ONa, is decomposed with a current of steam and CO<sub>2</sub> to liberate the phenol and the resulting vapor is condensed as fast as the phenol is formed.

**Synthetic glycerol.** K. P. McELROY. U. S. 1,466,665, Sept. 4. An oil gas rich in propylene is treated with a limited amt. of Cl to react selectively with the propylene but not with the C-H<sub>2</sub>, and the reaction product is recovered and further chlorinated to add another Cl atom to the mol. Glycerol is then produced from the Cl deriv. thus obtained, by heating under pressure with NaHCO<sub>3</sub> soln. or by heating with NaOAc and then with NaOH or NaHCO<sub>3</sub> soln.

**Triarylguanidines.** L. P. KYRIDES. U. S. 1,466,535, Aug. 28. A soln. of an aryl-amine and a diarylthiourea, e. g., PhNH<sub>2</sub> and thiocarbonylthiourea, is heated with an inert hydrocarbon solvent such as toluene which is immiscible with H<sub>2</sub>O, in the presence of PbO or other desulfurizing agent, while distg. off the H<sub>2</sub>O liberated by the reaction, in order to produce triarylguanidine, e. g., triphenylguanidine.

**Dehydrating ethyl ether and other organic liquids.** J. A. S. HAMMOND. U. S. 1,466,435, Aug. 28. Vapors of Et<sub>2</sub>O or similar liquid to be dehydrated are brought into contact with a dehydrating agent such as NaOH to remove most of the H<sub>2</sub>O and afterward given a final treatment with strictly anhyd. NaOH or other reagent to remove the last traces of H<sub>2</sub>O. U. S. 1,466,436 specifies the dehydration of Et<sub>2</sub>O in liquid condition by treatment with successive portions of NaOH, the last portion being anhyd.

**Bubble tower apparatus for manufacture of ether.** F. E. LICHTENTHALER. U. S. 1,467,583, Sept. 11. A series of conduits with capped plates are all enclosed within a pressure heating jacket.

**Urea.** ELEKTIZITÄTWERK LONZA. Brit. 196,601, April 11, 1923. In the prepn. of urea salts of mineral acids by the action of acids on solns. of cyanamide, the soln. of cyanamide is gradually added to the acid to avoid local heating and the consequent formation of undesirable by-products, such as dicyanodiamide.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**The significance of the calcium in the blood.** ERNST BILLIGHEIMER. *Klin. Wochschr.* 2, 1033-6(1923).—A review. MILTON HANKE

**The solubility of uric acid.** KARL HARPUDE. *Klin. Wochschr.* 2, 1268(1923).—Uric acid begins to ppt. from a phosphate buffer soln. as soon as the reaction becomes acid, i. e., below  $p_H$  6.8. A ppt. is not obtained in an acetate buffer soln. contg. 25 mg. % of uric acid until the  $p_H$  drops below 4.7 to 4.9. From a lactate buffer soln. uric acid begins to ppt. at  $p_H$  4.2-4.1 and is completely pptd. at  $p_H$  2.5. The addition of urea, glycine, dextrose, glycogen and serum albumin to a phosphate buffer soln. gives results similar to those obtained in the acetate and lactate buffer solns. These compds. inhibit the pptn. of uric acid. At  $p_H$  4.2, the solns. must contain 97.55% of uric acid and 2.45% of Na urate. The abnormally high soly. of uric acid in solns. contg. urea, glycine, dextrose, glycogen, serum albumin, acetates or lactates may be due to complex salt formation. MILTON HANKE

**The role of thrombin in the coagulation of blood.** EDGAR WÖHLISCH. *Klin. Wochschr.* 2, 1073-4(1923).—The isoelec. pt. of pure fibrinogen is at  $p_H$  4.86. Thrombin converts fibrinogen into a globulin that has an isoelec. zone in the region of  $p_H$  7.0. The globulin then ppts. out since this is the approx. reaction of the blood. Heat coagulation and coagulation by means of thrombin seem to be identical processes. Cf. C. A. 17, 571. MILTON HANKE

**Dehydrocholeic acid, an active, practically nontoxic member of the bile acid group.** ERNST NEUBAUER. *Klin. Wochschr.* 2, 1065-7(1923).—Guinea pig blood corpuscles, suspended in 0.85% NaCl, are hemolyzed by Na desoxycholeate (NaDo) at a concn. of 0.04% and by Na dehydrocholeate (NaD) at a concn. of 0.63%. NaD has no appreciable hemolyzing action when dissolved in serum. Surviving frog hearts are not injured by a 0.5% soln. of NaD. A 1% soln. reduces the contraction force only after 5-10 min. A 2% soln. rapidly reduces the contraction force of the heart and leads to complete inhibition in 10 min. A 1:1800 soln. of NaDo stops a surviving heart in 1 min. The minimum lethal dose of NaD, for guinea pigs, is 4.4 g. per kg. body wt. when injected subcutaneously. Dogs may tolerate doses of 0.43 g. per kg. body wt., intravenously, without discomfort. Man tolerates 2 g. intravenously, 3 times per day without discomfort, and without clinical symptoms. NaD is a powerful cholagog. It increases the rate of flow of the bile and the bile secretion pressure. It is recommended as a cholagog because of its low toxicity. MILTON HANKE



**Recent advances in science—Biochemistry.** R. KEITH CANNAN. *Science Progress* 18, 18-22(1923).—Review of recent work on carbohydrate metabolism and diabetes, enzymes, and biochem. oxidation. JOSEPH S. HEPBURN

**Premedical requirement in chemistry.** THEODORE HOUGH. *Proc. Annual Meeting Assoc. Am. Med. Colleges*, 33, 85-101(1923).—The present min. requirement (4 semester hrs.) in org. chemistry is inadequate and should be increased to a total of 8 hrs. of which at least 2 should be lab. work. At present only general and org. chemistry can be given in the 2 yrs. of collegiate premedical work; it is impractical to require quant. analysis and phys. chemistry. JOSEPH S. HEPBURN

**The increasing significance of permeability problems for the biological and medical sciences.** H. J. HAMBURGER. *Bull. Johns Hopkins Hosp.* 34, 173-81, 226-35, 266-73 (1923).—Lectures. Cf. C. A. 16, 1983. A. P. LOTHROP

**Nitrogen distribution in globin.** ANDREW HUNTER AND HENRY BORSOOK. *J. Biol. Chem.* 57, 507-14(1923).—Analytical data are presented which suggest that the globin mol. yields on hydrolysis 2 mols. of tryptophan, 4 each of tyrosine and arginine, 8 of histidine, 10 of lysine and approx. 100 other amino acid mols., including dicarboxylic acids. It contains 2.61% of tryptophan and 4.63% of tyrosine, which gives a mol. ratio that is exactly 1:2. The following av. % distribution of N in globin was found:  $\text{NH}_4$  5.37, humin 1.9, arginine 8.0, histidine 12.7, lysine 11.1, amino N of filtrate 57.0, non-amino N of filtrate 3.3, total N recovered 99.4. To obtain a globin of const. compn. from simple recrystn. of oxyhemoglobin, 3 crystns. at least are necessary; if a preliminary treatment with Al cream is employed, two crystns. will suffice. The mol. wt. is calcd. to be between 15,630 and 15,640, which agrees surprisingly with the 15,274 deduced by Osborne from the S content. A. P. LOTHROP

**An electrochemical study of hemoglobin.** J. B. CONANT. *J. Biol. Chem.* 57, 401-14(1923).—"The oxidation of hemoglobin to methemoglobin by  $\text{K}_3\text{Fe}(\text{CN})_6$  and the reduction of methemoglobin to hemoglobin by  $\text{Na}_2\text{S}_2\text{O}_4$  can be followed electrometrically. The change from reduced hemoglobin to methemoglobin involves only one H equiv. of oxidizing or reducing agent per g. mol. and has a definite oxidation-reduction potential. The potential of a mixt. of hemoglobin and methemoglobin is raised by passing in  $\text{O}_2$  or CO and lowered again by removing these gases completely. The potential of an inert electrode immersed in a hemoglobin soln. varies with the partial pressure of the  $\text{O}_2$  because the ratio of free hemoglobin to methemoglobin is varied by the degree of oxygenation. The change of hemoglobin to oxyhemoglobin is one involving oxygenation and not oxidation. By representing hemoglobin as the Na salt of a complex ferro acid, the relationships indicated by the present work can be adequately expressed and the analogy between hemoglobin and Manchot's amino-ferrocyanides (C. A. 7, 739; 8, 634) emphasized. Preliminary expts. with hematin seem to indicate that the reduction of this substance to hemochromogen involves the addn. of 2 H atoms. If this be so, the relationship between this pair of compds. has no bearing on the problem of the oxidation or oxygenation of hemoglobin." A. P. LOTHROP

**The action of proteolytic enzymes upon insulin.** E. J. WITZEMANN AND LAURA LIVSHIS. *J. Biol. Chem.* 57, 425-35(1923).—Insulin preps. are completely inactivated by the proteolytic enzymes, trypsin, papain and pepsin. This fact would indicate that the compds. present in the preps. of insulin that give the qual. reactions for protein are not all impurities but that insulin itself is protein-like in character. It is suggested that the "insulin effect" is associated with a certain group or grouping which may be protein on the one hand and peptone or polypeptide on the other so that its qual. reactions will range all the way from a negative biuret reaction for the simplest group that still retains the characteristic properties of insulin to those of a typical protein. If this interpretation of the known facts concerning insulin is correct, it does away with the contradictions concerning its nature in the literature (Doisy, Somogyi, and Shaffer, C. A. 17, 3680; Best and Macleod, *Proc. Am. Soc. Biol. Chemists*, *J. Biol. Chem.* 55, xix) and conforms with the new data obtained in the present expts. A. P. LOTHROP

**The kinetics of the conversion of creatine into creatinine in hydrochloric acid solutions.** GRAHAM EDGAR AND R. A. WAKEFIELD. *J. Am. Chem. Soc.* 45, 2242-5 (1923).—The rate of conversion of creatine into creatinine in the presence of HCl as a catalyst has been measured for concns. of acid between 0.19 N and 40.76 N and for a temp. range of 25-100°. The general nature of the reaction, and the influence of temp. and acid concn. are discussed. Cf. C. A. 17, 3196. H. M. McLAUGHLIN

**The reaction of proteins with soaps and fatty acids.** I. S. MATSUMURA. *Kolloid Z.* 32, 173-6(1923).—Expts. with dialyzed horse serum and equal vols. of Na oleate solns. show pptn. of all serum albumin, pseudoglobulin and euglobulin. Oleic acid causes no pptn. Pptn. is not complete but becomes complete when the alkali formed is

removed. On heating to 56° serum pptd. with NaCl dissolves but dialyzed pure serum is not pptd. by soap. A. MUTSCHILLER

**Sucrase.** E. CANALS. *Bull. soc. chim.* 31, 1333-41(1922); cf. C. A. 17, 570.—Analyses of certain sucrase preps. showed that the more active the sucrase, the greater was its content of Mg and of  $P_2O_5$ . However, dialysis increased the activity but decreased the quantities of these elements; and pptn. by alk. decreased both the activity and the content of Mg and of  $P_2O_5$ . Therefore, C. believes that sucrase activity is not dependent on the content of Mg and  $P_2O_5$ , although the former was always held more tenaciously than the latter. J. J. WILLAMAN

Oxidation of carbohydrates (STIEGLITZ) 10.

## B—METHODS AND APPARATUS

STANLEY K. BENEDICT

A method for the determination of bilirubin in urine. BERTHOLD ZINS. *Klin. Wochschr.* 2, 978(1923).—The method is based upon that of Vogl and Zins (cf. C. A. 17, 2011) for the detn. of bilirubin in blood. The urine is treated with 3-5 drops of a 1% soln. of  $NaNO_2$  and then with a few crystals of  $BaCl_2$ . The ppt. is collected on a small filter. The paper plus ppt. is spread out and treated with a few drops of a 20% soln. of  $CCl_3COOH$ . Traces of bilirubin evoke a pale green color. With larger amts. the color is a deep blue green. MILTON HANKE

Quantitative estimation of urobilin. (Criticism and improvement of the method of Adler.) OPITZ AND BREHME. *Klin. Wochschr.* 2, 1269(1923).—The improvements consist of a standardization of the light source used in detg. the fluorescence of the Zn salts, a Soxhlet extn. of the feces in place of the repeated agitations, and the use of spirit in place of abs. alc. MILTON HANKE

Note on the estimation of urea by urease. G. M. WISHART. *Biochem. J.* 17, 403(1923).—The estn. of urea can be carried on more rapidly and easily by hydrolyzing the urea and evacuating the formed  $NH_3$  simultaneously. An arrangement of app. and the necessary procedure are described for accomplishing this. B. HARKOW

Clinical applications of micro-methods in blood analysis. I. S. KLEINER. *Hahnemannian Monthly* 58, 581-5(1923).—A description of the Kleiner colorimeter and its use in the detn. of blood sugar. For clinical purposes, the sugar content of venous and capillary (finger) blood is the same. JOSEPH S. HEPBURN

Estimation of the amount of pancreatic enzymes in duodenal fluid by a modified Gaultier's method. GEO. F. SPENCER. *J. Lab. Clin. Med.* 8, 741-4(1923).—A slight variation of the usual methods. suitable for rapid clinical work. Gelatin is used as the substrate in the estn. of tryptic activity. E. R. LONG

Adaptation of Shaffer's titration method for blood sugar to clinical use. H. D. HASKINS AND WM. P. HOLBROOK. *J. Lab. Clin. Med.* 8, 747-51(1923).—A modification of the Shaffer method (C. A. 15, 1328), the essential feature of which is checking of the thiosulfate against the Cu reagent. By this adjustment of the soln. the control estn. of the reagent is always 19.5 cc. of dil. thiosulfate. A table is given from which the percentage of glucose in the blood can be read without calcn. E. R. LONG

An aeration apparatus for the determination of urea in blood. A. T. WEATHERS AND H. C. SWENY. *J. Lab. Clin. Med.* 8, 752-4(1923).—A modification of the Polin-Wu technic by an app. in which 8 samples may be aspirated simultaneously. E. R. L.

A substitute for acid hematin as the standard in Sahli's hemoglobinometer. L. D. FELTON. *Bull. Johns Hopkins Hosp.* 34, 357-9(1923).—The product obtained by oxidizing pyrogallallic acid in alk. soln. gives a color which is the same as that of acid hematin and maintains a const. color tint over a long period. The product is prepd. as follows: Make a 10% soln. of pyrogallallic acid in 75% alc. and add enough 40% NaOH soln. to make a 10% soln. of the NaOH in the 75% alc. Oxidize by bubbling air through the mixt. as long as a ppt. is formed (overnight is sufficient). Decant the supernatant liquid and dissolve the tarry residue in  $H_2O$ . Ppt. again with 75% alc. and continue this treatment until the product becomes neutral or at least is not strongly alk. Finally wash with 95% alc., spread out in a thin layer and leave in the air until the odor of alc. has disappeared. Dry in  $H_2SO_4$  desiccator and grind to a fine powder. In making the standard dissolve the powder in a Sørensen phosphate buffer mixt. of  $pH$  6. The soln. of the powder matches acid hematin very closely down to a value representing 60%. A. P. LOTHROP

A study of the inorganic elements of blood plasma. A. P. BRIGGS. *J. Biol. Chem.* 57, 351-7(1923).—A system of analysis is presented which permits the detn. of Na, K, Ca, Mg, chlorides and phosphates on a single small sample of blood. Draw blood from superficial veins of the forearm and transfer it to a 50-cc. centrifuge tube

contg. about 3 mg. of Li citrate per cc. of blood. Centrifuge at high speed for a few min. and draw off the plasma. Measure 9-15 cc. of the plasma, the amt. required for a complete analysis, by a Folin-Wu pipet into an Erlenmeyer flask, dil. with 3 vols. of  $H_2O$  and ppt. the protein with an equal vol. of 20%  $CCl_3CO_2H$ . Shake vigorously for a min., allow to stand for 10 min. and filter. **Sodium:** Evap. 5-10 cc. of the filtrate with 5 cc. of concd.  $HNO_3$  to dryness on a steam bath in a 50-cc. glass evapg. dish. Dissolve the residue in 2 cc. of distd.  $H_2O$  and det. the Na according to the method of Kramer and Tisdall (*C. A.* 15, 2461). The necessity of prepg. an antimonate reagent, 10 cc. of which are equiv. to about 11 mg. of Na, is especially emphasized; different samples of antimonate are apt to vary greatly in their Sb content. **Ca and Mg:** Neutralize 15 cc. of the filtrate with  $NH_4OH$  using methyl red as indicator, ppt. the Ca as oxalate, filter, wash and titrate the ppt. according to the technic of Simpson (*C. A.* 16, 215). Det. the Mg on the Ca filtrate according to the method of Briggs (*C. A.* 16, 2701). **Phosphates:** Use Briggs' modification of the Bell-Doisy procedure (*C. A.* 16, 3493). **Chlorides:** Adapt the method of Whitehorn (*C. A.* 15, 1323) to the  $CCl_3CO_2H$  filtrate. **Potassium:** Add 3-4 drops of concd.  $HNO_3$  to 5 cc. of the filtrate in a small glass evapg. dish and evap. to dryness on a steam bath. Dissolve the residue in 1 cc. of distd.  $H_2O$ , add 2 cc. of the cobaltinitrite reagent and set aside 4 hrs. for pptn. Filter on a Gooch crucible prepd. as follows: Pour into the Gooch crucible enough paper pulp to make a mat about 1 mm. thick, cover with a piece of filter paper and press the whole mat down flat and tight. Wash out the dish 4 times with 3 cc. portions of 10% NaCl, passing each through the Gooch crucible; then wash the crucible twice with 3 cc. of the NaCl soln. Pick out the mat and drop it back into the dish contg. the rest of the ppt., add about 20 cc. of approx. 0.1 N NaOH and heat to boiling. Wash the soln. into a graduated cylinder, dil. with  $H_2O$  to 100 cc., and mix. Transfer an aliquot of this soln. equiv. to about 0.01 mg. of K (5 cc. where 5 cc. of the  $CCl_3CO_2H$  filtrate were used) to a 100 cc. volumetric flask. To another 100 cc. flask transfer 5 cc. of the standard nitrite soln. To each add 70 cc. of distd.  $H_2O$ , 2 cc. of the sulfanilic acid soln. and 1 cc. of the naphthylamine soln. Dil. to 100 cc., mix, and compare in a colorimeter after 5 min. **Reagents:** K soln.: dissolve 0.382 g. of pure KCl or 0.445 g. of  $K_2SO_4$  in 1 l. of distd.  $H_2O$  to give a soln. contg. 0.2 mg. of K per cc. Cobaltinitrite reagent: dissolve 220 g. of  $NaNO_2$  in 400 cc. of  $H_2O$  and 113 g. of Co acetate in 300 cc. of  $H_2O$ . Mix the solns. and add 100 cc. of glacial AcOH. Pass a current of air through the reagent for several hrs. to remove the nitric fumes, filter, and keep in a glass-stoppered bottle in an ice box. \*Standard nitrite soln.: prep. a stock soln. of 1.5 g. of  $KNO_2$  in 1 l. of  $H_2O$  and make the standard from this by dilg. 10 cc. to 1 l.; to standardize it, take 2 cc. of the K soln. (equiv. to 0.04 mg. of K) in a small beaker, ppt., wash, decompose with NaOH, and make up to 200 cc. as in the detn.; compare 5 cc. of this soln. (equiv. to 0.01 mg. of K) with 5 cc. of the standard nitrite soln. according to the technic of the detn. and thus obtain the value of the nitrite standard in terms of its K equiv. Sulfanilic acid and  $\alpha$ -naphthylamine solns.: 0.5% soln. in 30% AcOH. Filter papers: treat a package of 11 cm. filter papers with dil.  $HNO_3$  for about 1 hr. in a large dish to remove any salts and HCl, wash repeatedly by decantation and dry. **Results:** The following av. results were obtained in mg. per 100 cc. of plasma: P 2.9, Cl 355, Na 317, K 19.6, Ca 9.6, Mg 2.5, values very close to those given as av. normal for human serum or plasma. The equiv. normality of the bases was found to be 0.15 and for the acids 0.1259, giving an excess of bases of 16%. Except in nephritis marked variations in the level of inorg. elements of blood are quite exceptional.

A. P. LOTHROP

**Concentration of insulin by adsorption on benzoic acid.** P. J. MOLONEY AND D. M. FINDLAY. *J. Biol. Chem.* 57, 359-61 (1923).—The concn. of dil. aq. solns. of insulin is expensive and loss of potency results so that the possibilities of adsorption have been investigated. When finely divided BzOH is pptd. it carries down with it a large % of potent material which can readily be recovered from the ppt. The method is as follows: To 1 l. of a crude aq. ext. (such as the concentrate from the original alc. ext. of pancreas) add 50 cc. of a 25% BzONa soln. and acidify by adding 12.5 cc. of concd. HCl, which is sufficient to sat. the soln. and give a lasting ppt.; the amts. can be varied proportionately if necessary to give the first lasting ppt. Add 40 cc. more of the BzONa soln. and 10 cc. of concd. HCl and filter after allowing sufficient time for complete pptn. This ppt. usually contains about  $\frac{1}{2}$  of the potent material. Treat the filtrate again with the same amts. of BzONa and HCl for a second pptn. A third pptn. may be carried out if the filtrate still contains sufficient potent material. Filter and wash the ppt. with a satd. aq. soln. of BzOH. The small amt. of active material removed by washing can be recovered by pptn. If the original soln. was comparatively free from protein, treat

the  $\text{BzOH}$  ppt. with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$  to form two layers in a separatory funnel and the potent material will pass into the  $\text{H}_2\text{O}$  layer. Wash the  $\text{H}_2\text{O}$  layer with  $\text{Et}_2\text{O}$  to remove traces of  $\text{BzOH}$  and then boil the aq. soln. *in vacuo* to remove the dissolved  $\text{Et}_2\text{O}$ . If the original soln. was grossly impure, make up the moist ppt. to 80% with  $\text{EtOH}$  and allow to stand in an ice box. Filter off the ppt. which settles out. Conc. the filtrate *in vacuo* and ext. with  $\text{Et}_2\text{O}$  as previously described. A. P. LOTHROP.

**The refractometric determination of hemoglobin.** J. I. STODDARD AND G. S. ADAIR. *J. Biol. Chem.* 57, 437-54 (1923).—(1) Measure two 1 cc. samples of blood into 2 medium size test-tubes. (2) To one sample add 5 cc. of 0.8%  $\text{NaCl}$ . (3) To the other sample add 5 cc. of 0.8%  $\text{NaCl}$  contg. about 70 mg. of saponin per 100 cc. (4) Centrifuge (2) and (3) and read the clear solns. in an immersion refractometer. Read the two salt solns. also. Calcs.: Subtract the refractive indices of the two salt solns. to obtain the added refraction due to the saponin. Multiply by 5/5.6 to get the diln. of the saponin refraction by the added 0.6 cc. (approx.) of plasma. Subtract this saponin correction from (3) and then subtract (2) from the result to obtain the increase due to the hemoglobin. Divide by the hemoglobin factor, 194.2, and multiply by 6 (the diln.) to get the concn. of hemoglobin in the original blood in terms of dry wt. in g. per 100 cc. Of course the  $n$  of the  $\text{NaCl}$  and saponin solns. need not be detd. for every detn. but the saponin tends to ppt. with age and should be checked up from time to time. The results are about 0.25% too high. It is usually necessary to clean the refractometer prism before reading; the prism should be left in the soln. about 3 min. to allow it to attain the temp. of the soln.; then it is quickly cleaned by wiping the face with moist and then with dry lens paper, which will not alter the temp. of the whole prism, and is read in  $1/2$  min. The greatest sources of error are volumetric technic, temp. control, and adjustment of the compensating prism; no reading should be made unless the line is perfectly clear and sharp. The temp. at which the solns. are read should not vary more than  $0.15^\circ$  or else correction must be made for the difference in temp. The blood should be obtained with paraffin oil to avoid hemolysis. To prevent the oil mixing with the blood as would occur if the sample were shaken previous to measuring, place the blood in a test-tube, allow the oil to rise to the top, pipet it off, and then mix by introducing a large-bored pipet so that the tip is near the bottom of the test-tube and draw the blood up and down rapidly. This method compared with the  $\text{O}_2$  capacity of the same blood obtained by the Van Slyke method gives a ratio of 1.26 as compared with Hufner's of 1.34. If the  $\text{O}_2$  capacity was obtained by the Haldane method the ratio would be about 1.15, indicating the greater accuracy of the Van Slyke method. The refractive const. "a" for human hemoglobin, detd. on pure hemoglobin solns. the concn. of which was obtained by getting the dry wt. at  $110^\circ$ , was found to be 194.2. This compares with 183 found by Howard (*C. A.* 14, 1684) on cryst. horse hemoglobin and, if the substances are comparable, would indicate 5.7% of water of crystn. A. P. LOTHROP.

**Lead studies. VII. The microchemical detection of lead.** L. T. FAIRHALL. *J. Biol. Chem.* 57, 455-61 (1923).—The test depends upon the formation of a hexanitrite of  $\text{K}$ ,  $\text{Cu}$  and  $\text{Pb}$ — $\text{K}_2\text{CuPb}(\text{NO}_2)_6$ —which can be readily identified under the microscope as black regular rectangular plates or cubes. 0.001 mg. of  $\text{Pb}$  may be sepd. and readily identified from 15 cc. of a soln. contg. other salts. Definite but very small amts. of reagents must be used and capillary pipets should be prepd. by drawing out 4 mm. tubing to a capillary and blowing a bulb at one end; the stem should be roughly calibrated by marking 2 points representing a vol. of 5 cu. mm. (about  $1/10$  of a normal drop). If org. material is being tested, bake and ash and dissolve the ash completely in  $\text{HCl}$  (*C. A.* 16, 2160), having the vol. of the soln. about 25 cc. Neutralize the soln. and then make it just acid to methyl orange with dil.  $\text{HCl}$ . Add 1 cc. of satd.  $(\text{NH}_4)_2\text{SO}_4$  soln. and 1 drop of 2%  $\text{Cu}$  acetate and sat. the cold soln. with  $\text{H}_2\text{S}$ . Centrifuge and wash at least 3 times by decantation, draining the  $\text{H}_2\text{O}$  completely from the ppt. each time by means of a capillary tube. The washing must be thorough and the wash water completely removed each time as small amts. of inorg. salts seriously interfere with the test. Place the centrifuge tube in a beaker of boiling  $\text{H}_2\text{O}$  and add 2 drops of  $\text{HNO}_3$ . Draw some of the soln. into a capillary tube and evap. a drop or so to dryness on a microscope slide. Add 5-10 cu. mm. of 4%  $\text{AcONa}$  soln. and dissolve the residue completely. Collect the material into 1 droplet and evap. to dryness. Chill the slide on ice; then add 5 cu. mm. of 10%  $\text{AcOH}$  and place a small crystal of  $\text{KNO}_3$  in the center of the residue so that it will diffuse to the outer edge. Exam. microscopically for the small black cubes or squares which are usually found in the outer rim scattered among the crystals of  $\text{Cu}$  acetate. If the presence of  $\text{Bi}$  is suspected ( $\text{Bi}$  salts are occasionally administered in cases of  $\text{Pb}$  poisoning), it must be removed since it prevents the formation of the hexanitrite crystals. Evap. the  $\text{HNO}_3$  soln. of the nitrates to dryness in the centrifuge tube

and then add 1-2 drops of  $H_2O$ , which ppts. white Bi oxynitrate. Drop into the soln. a fine capillary tube having a tiny plug of cotton at one end. The clear liquid is drawn into the tube by capillary action and a drop may be transferred to a slide after breaking off that part of the tube contg. the plug. The reagents must be free from Pb and may be purified as follows: Sat. the cold satd.  $(NH_4)_2SO_4$  soln. with  $H_2S$ , allow to stand overnight, filter and boil out the excess of  $H_2S$ . Prep. pure  $KNO_3$  from  $AgNO_3$  by adding  $AgNO_3$  to a filtered soln. of  $KNO_3$ ; filter, wash the  $AgNO_3$  well with cold  $H_2O$ , dissolve in boiling  $H_2O$ , add an equiv. amt. of pure KCl, and crystallize the pure  $KNO_3$  in soln. by evapp. to a small vol. Acids and  $NH_4OH$  may be purified by the methods devised by Lenz (*C. A.* 7, 1148). A. P. LOTHROP

The accuracy of the "ionometric" method and of the protein correction in measuring serum conductivity. H. C. GRAM AND G. E. CULLEN. *J. Biol. Chem.* 57, 477-481 (1923).—"The ionometric method of Christiansen (*C. A.* 16, 4231) for measuring cond. of electrolytes ordinarily agrees with the Kohlrausch method to within 1% and with a max. difference of 2%. Urea or glucose in the highest concn. possible in serum causes negligible depression of cond. and negligible change in  $n$ . The depression of cond. due to protein has been found to be the same with the ionometric and with the Kohlrausch method. Our av. value of 2.2% per 1% of protein agrees with the values reported by other observers. Serum cond. values should be corrected to a protein-free basis. The refractometer method of detg. the protein concn. is adequate for this purpose." A. P. LOTHROP

A micro method for the determination of the hydrogen-ion concentration of whole blood. J. A. HAWKINS. *J. Biol. Chem.* 57, 493-5 (1923).—"The method is a slight modification of that recently described by Cullen (*C. A.* 16, 2700) and requires only 0.6 cc. of blood, thus rendering it possible to make repeated detns. on small lab. animals. Add 30 drops of a 0.03% soln. of phenol red to 50 cc. of a 0.9% NaCl soln. and adjust to  $p_H$  7.3. Place 5-cc. portions of this soln. in tubes with a diam. of 16 mm. and cover with paraffin oil. Draw the blood directly from the heart or vein into a 1 cc. pipet, graduated in  $1/100$ , by attaching a needle with a short rubber tube to the pipet. Run 0.25 cc. of the blood under the oil in one of the tubes contg. the saline indicator soln. and mix thoroughly by stirring carefully with a clean glass rod. Centrifuge for 10 min. Place the tube in a comparator block and det. the  $p_H$  by matching the nearest color standard and applying corrections as described by Cullen. The standard color tubes are 16 mm. in diam. and contain 5 cc. of Sørensen's standard phosphate solns. ranging in steps of 0.05  $p_H$  from  $p_H$  7.00 to 7.80. The max. deviation between the method and the original was 0.03  $p_H$  and in most cases there was practical agreement. The total  $CO_2$  content may also be detd. by Van Slyke's method, using 0.2 cc. of the excess blood in the pipet. A. P. LOTHROP

A quantitative color reaction given by adrenaline and urine. HERMAN FRIEND. *J. Biol. Chem.* 57, 497-505 (1923).—"Adrenaline reacts with sulfanilic acid and  $HNO_3$  to give a red color in the presence of  $NH_4OH$  and this color is quant. proportional to the adrenaline concn. The phenols present in urine give the same color but the adrenaline can easily be removed by a suspension of  $Fe(OH)_3$  in  $H_2O$  so that the amt. of adrenaline (or of substance reacting like adrenaline) can be estd. by the decrease in the color of the urine after treatment with  $Fe(OH)_3$ . None of the common inorg., org., and pathol. urinary constituents gave a positive reaction before treatment with  $Fe(OH)_3$  and a negative reaction after it so that it appears possible that the urinary constituent giving the color before, but not after, the  $Fe(OH)_3$  treatment is adrenaline. Normal urines gave a usual reaction equiv. to 0.2 to 0.4 mg. per 100 cc. of this substance. Adrenaline reduces Benedict's, Fehling's, and Nylander's solns. and it seems possible that slight reductions occasionally observed in glucose-free urines may be due to the adrenaline present. The original should be consulted for the details of the detn. A. P. L.

The application of the quinhydrone electrode to electrometric acid-base titrations in the presence of air, and the factors limiting its use in alkaline solution. V. K. LA MER AND T. R. PARSONS. *J. Biol. Chem.* 57, 613-31 (1923).—"Precise electrometric titrations designed to det. the limits of reliability of the benzoquinhydrone electrode as a means of detg.  $p_H$  (Büllmann, *C. A.* 16, 1697) have been carried out on HCl, AcOH, boric acid and  $KH_2PO_4$ . Reliable results are obtained in buffered solns. more acid than  $p_H$  8.0 and the method can be substituted for the H electrode in such cases, provided no rapid oxidizing or reducing agents are present. In more alk. solns. autooxidation of hydroquinone and the effect of the presence of hydroquinone on the actual  $p_H$  in unbuffered alk. solns., owing to its weak acid properties, are more important factors in yielding erroneous results than are the very small errors which are produced by the deviations from the simple Peters' oxidation-reduction potential equation owing to

partial ionization of hydroquinone. The benzoquinhydrone electrode can be substituted for the H electrode as a more simple and more rapid way of accurately detg. the titration end-points of acids (but not of bases) that are stronger than the secondary ionization const. of  $H_2PO_4$ .

A. P. LOTHROP

**A new method of decalcification.** C. P. WHITE. *J. Path. Bact.* 26, 425(1923).—A satd. aq. soln. of citric acid is dild. 1 to 10 with water. A little methyl red and a little  $\alpha$ -naphtholphthalein are added and then enough  $NH_4OH$  to produce a clear yellow color. Add a little  $CHCl_3$  as a preservative. The fluid does not harm tissues or staining properties.

JOHN T. MYERS

**Quantitative determination of enzyme activity in duodenal fluids.** C. W. LUDDEKS AND M. E. REHFUSS. *Am. J. Med. Sci.* 166, 535-8(1923).—The tryptic, lipolytic, and amylolytic activities of duodenal contents are detd. by measuring the extent of the reactions occurring when the fluid is added to gelatin, olive oil, and sol. starch. The methods described are considered sufficiently accurate for clinical work.

G. H. S.

**Improved formula for a testing ink for sterilizers and autoclaves.** IVOR GRIFFITH. *J. Am. Pharm. Assoc.* 12, 139-40(1923).—Triturate 3 g. of carmine with 120 cc. of 26%  $NH_4OH$  until dissolved, add 30 g. of finely powd.  $AgNO_3$ , stir, add 30 g. of  $KHC_4H_4O_6$ , stir again, add 15 cc. of sirup, stir and add 15 cc. of mucilage of acacia. Shake thoroughly. A dark red mixt. results which writes light red. In each batch of material to be sterilized a card is placed on which characters have been written with the ink. If a temp. of  $127^\circ$  at 20 lb. pressure has been reached during the sterilization the writing will be an intensely black color.

L. E. WARREN

Estimation of small quantities of Ca (LAIDLAW, PAYNE) 7.

#### C—BACTERIOLOGY

A. K. BALLS

**The growth of yeast on a medium of wholly synthetic origin.** E. I. FULMER, V. E. NELSON AND ANNE WHITE. *J. Biol. Chem.* 57, 397-9(1923); cf. *C. A.* 15, 604, 2465; 16, 2347.—Continuous growth of yeast has been shown to be possible on media composed of salts and cane sugar but the fact that one of the constituents of the media, cane-sugar, is of natural origin leaves open to criticism any definite conclusions in regard to the need of bios for the growth of yeast. In the present expts. yeast has been grown in a medium contg. 2 g. of "methose," 0.188 g. of  $NH_4Cl$ , 0.1 g. of  $K_2HPO_4$ , 0.1 g.  $CaCl_2$ , and 0.04 g. of  $CaCO_3$  per 100 cc. The final dild. of the original yeast was about  $1:10^{11}$  and the greatest possible "carry over" about  $1:10^8$ . "There can be no question that the yeast was growing only on the constituents of the medium and, therefore, that the success in the subculture of yeast on cane-sugar could not have been due to traces of impurities unless the same or similar impurities were synthesized along with the methose." The methose (first prepd. by Loew, *Ber.* 22, 470(1889)) was prepd. as follows: formalin was acidified with  $H_2SO_4$  and distd. The distillate was made up to contain per l. 10 g. of  $HCHO$ , 0.125 g. of  $MgO$ , 0.5 g. of  $MgSO_4$  and 75 g. of granulated Pb. It was heated on a water bath at  $65-70^\circ$  for a day or two until the odor of  $HCHO$  had entirely disappeared. After filtering off the Pb, the liquid was evapd. *in vacuo* to small vol., made up to 80%  $EtOH$  and the Pb and Mg salts were pptd. out with  $CO_2$ . After filtration the liquid was evapd. on a water bath. The resulting material was a colorless or slightly yellow sirup which was used in the expts. as a source of C and energy as a substitute for cane-sugar.

A. P. LOTHROP

#### D—BOTANY

H. M. DUGGAR

**The influence of solution volume upon plant growth in relation to reaction change and iron availability in culture solutions.** R. M. BARNETTE AND J. W. SHIVE. *Soil Science* 15, 413-25(1923); cf. following abstr.—Wheat plants were grown in vols. of 250, 500, 1000 and 2000 cc. of the Tottingham soln.  $T_1^2 C_1$  at an osmotic concn. of 1 atm. and in a modification of this soln. in which  $(NH_4)_2SO_4$  was substituted for the  $KNO_3$  in equiv. osmotic concn. Young wheat plants, not over 3 per culture, were grown in vols. of not less than 1000 cc. of the Tottingham soln. without retardation of growth if the solns. were renewed at least every 3 days and if a suitable amt. of Fe was supplied to prevent chlorosis. With the modified soln. contg.  $(NH_4)_2SO_4$ , the growth of plants varied in the order of the soln. vols. H-ion concns. were decreased rapidly by the plants in the Tottingham soln. at all stages. In the modified soln. the plants increased the H-ion concn. slightly during the early stages and decreased it during the later stages. This reversal in direction of reaction change suggests an important physiological change in the plants with respect to  $NO_3$  and  $NH_3$  requirements. Rate of reaction change was

detd. by vol. of the culture soln. The availability of Fe was detd. mainly by the reaction of the soln. R. BRADFIELD

The influence of volume upon the rate of change in the hydrogen-ion concentration of nutrient solutions in contact with plant roots and the effect of this change upon iron availability. R. M. BARNETTE. N. J. Sta., *Rept.* 1921, 345-7; cf. preceding abstr.—Expts. are reptd. upon the growth of wheat in Tottingham 4-salt soln. and a modification of this soln. by substitution of  $(\text{NH}_4)_2\text{SO}_4$  for  $\text{KNO}_3$ . The plants were grown in culture bottles of 250 to 2000 cc. capacities. Fe was added as  $\text{FePO}_4$  at the rate of 5 mg. per l. Single plants were grown for 36 days in each bottle and culture solns. renewed at intervals of 3.5 days. The greatest growth was made in the largest bottles. The H-ion concn. became less as growth proceeded. The original nutrient solns. had a  $p_{\text{H}}$  value of 4.7. After 36 days growth the av. was about  $p_{\text{H}}$  7.0. Chlorosis appeared about the 20th day. The yields from the Tottingham soln. were lower than with the modified soln. M. S. ANDERSON

Recent advances in science.—Plant physiology. WALTER STILES. *Science Progress* 18, 27-34(1923).—Review of recent work on assimilation. Cf. C. A. 17, 1492. JOSEPH S. HEPBURN

Synthesis and hydrolysis of starch under the influence of the anions of salts in plants. W. S. ILJIN. *Biochem. Z.* 132, 511-25(1922).—The salts promote the formation of enzymes and the activation of zymogens. JOSEPH S. HEPBURN

Physiological protection of plants from the injurious action of salts. W. S. ILJIN. *Biochem. Z.* 132, 526-42(1922).—The toxic action of salts upon plants may be prevented by the antagonistic action of certain ions, e. g., Ca, Na. The existence of halophytes is thus made possible. JOSEPH S. HEPBURN

Influence of conditions upon the life and development of marine algae. E. PEN-TANELLI. *Arch. sci. biol.* 4, 21-87(1923); *Physiol. Abstracts* 8, 81.—In unchanged sea water development of marine algae is stopped by a deficiency of  $\text{CO}_2$ , N and P. An increase in the concn. of the water is more favorable to growth than its diln. The smallest amts. of acids and alkalies exert a harmful effect; nitrates produce vigorous development, phosphates a rapid formation of reproductive organs. Na, Mg, O, and the sulfate ion are indispensable; K and Ca are useful; and Br, I, Li, Fe, and Mg exert a markedly stimulating action. JOSEPH S. HEPBURN

The applicability of vital stains for the determinations of the plasma reaction. W. RUHLAND. *Ber. botan. Ges.* 41, 252-4(1923).—The reaction of living plasma to "vital stains" is indefinite and can only be estd. approx. The colors are influenced by the presence in the plasma of neutral salts and of amphoteric colloids. A. L.

Influence of temperature, moisture and oxygen on the spore germination of *Ustilago avenae*. EDITH S. JONES. *J. Agr. Research* 24, 577-91(1923).—The min. temp. for germination of the spores of *U. avenae* is between 4 and 5°, the optimum between 15 and 20° and the max. between 31 and 34°. Moisture influences spore germination in such a way that it was found to be highest in a soil contg. 30% of its moisture-holding capacity, to fall off slightly at 60% and very markedly at 80%. The spores failed to germinate in a suspension exposed to an O-free atm. Influence of temperature on the spore germination of *Ustilago zeae*. *Ibid* 593-7.—The optimum temp. for *U. zeae* lies between 26 and 34°, the max. between 36 and 38° and the min. at a temp. of 8°. W. H. ROSS

Plant incrustations. ERICH SCHMIDT and A. MIERMEISTER. *Ber.* 56B, 1438-40(1923); cf. C. A. 17, 1822.—By the use of methods previously described, involving digestion with  $\text{ClO}_2$  soln., there was obtained from *Laminaria hyperborea* and *Fucus serratus*, resp., the following amts. of substances: skeleton materials, 19.5% and 26.8%; incrusting material destroyed by  $\text{ClO}_2$ , 3% and 6%; polysaccharides, 10.2 (ash content 20-22) and 21.5 (ash content 20-25)%. J. J. WILLAMAN

#### E—NUTRITION

PHILIP B. HAWK

##### NORMAL

Age and chemical development in mammals. C. R. MOULTON. *J. Biol. Chem.* 57, 79-97(1923).—Data are presented for the  $\text{H}_2\text{O}$ , ash and N content, on a fat-free basis, of cattle, guinea pigs, men, swine, dogs, cats, rabbits, rats and mice at different periods of life. All show a rapid decrease in  $\text{H}_2\text{O}$  and increase in ash and N content from earliest life until chem. maturity is reached, when the change becomes suddenly less and nearly const. compn. is reached. Chem. maturity is reached after approx. 4.5% of the total life cycle. Animals differ in compn. at birth, according as they are more or less mature. T. CERNOWALD

**Beriberi and deficiency diseases.** A. SCALA. *Ann. igiene* 29, Pt. V, 32 pp. (1919); *Bull. Agr. Intelligence* 11, 529-32 (1920).—Vitamins are considered to be colloidal complexes composed in part of inorg. compds.

JOSEPH S. HEPBURN

**Metabolism of cholesterol.** I. **Changes in the cholesterol content of the surviving liver of the normal dog.** C. AKTOM. *Arch. intern. physiol.* 20, 162-91 (1922); *Physiol. Abstracts* 8, 17 (1923).—The surviving liver apparently can both produce and destroy cholesterol. If artificial circulation be maintained for at least 1.5 hrs., the cholesterol content of the surviving liver increases if it was obtained from a fasting dog, and decreases if it was removed from a dog during active digestion or from a fasting dog into whose duodenum dil. HCl had been introduced. However, in the latter case, addn. of emulsified neutral fat to the perfusion liquid increased the cholesterol content of the liver. II. **The cholesterol balance in the surviving dog liver after extirpation of the pancreas.** *Arch. intern. physiol.* 20, 192-201 (1922); *Physiol. Abstracts* 8, 17.—The results just noted are not altered by previous extirpation of the pancreas; and that organ apparently does not play a prominent part in the metabolism of cholesterol.

JOSEPH S. HEPBURN

**Value of sweetened condensed milk as a food for babies.** MAX WOLF AND C. P. SHERWIN. *Arch. Pediatrics* 40, 397-402 (1923).—Expts. were made on groups of 7 babies each, feeding raw milk, pasteurized milk, and sweetened condensed milk, resp. Bone and tissue development proceeded equally well on all 3 diets. The condensed milk did not give rise to poor absorption of protein, or excessive gas fermentation.

JOSEPH S. HEPBURN

**The identity or non-identity of antineuritic and water-soluble B vitamins.** P. A. LEVENE AND MARIE MUELFELD. *J. Biol. Chem.* 57, 341-9 (1923).—Certain samples of yeast used as a source of vitamin B which were sufficiently active to maintain normal growth in rats failed to protect pigeons fed on polished rice from polyneuritis although the vitamin B content of the yeast samples varied comparatively little. Two samples of yeast protected pigeons in doses of 0.5 g. per day; a third gave irregular results in doses of 1 g. per day and a fourth failed to protect even in doses of 2 g. per day. These results give additional evidence in support of the view that the antineuritic and the growth-promoting principle are not identical but "it must be borne in mind that the final solution of the problem will be furnished only by the knowledge of the chem. nature of the active principles."

A. P. LOTHROP

**Biochemical studies on allantoin.** I. **The influence of amino acids on the excretion of allantoin by the rabbit.** A. A. CHRISTMAN WITH H. B. LEWIS. *J. Biol. Chem.* 57, 379-95 (1923).—"The feeding of amino acids (glycocoll, alanine and glutamic acid) to rabbits was followed by a marked decrease in the daily elimination of allantoin. Similar results were obtained after enteral administration of large amts. of gelatin. The changes observed, however, were neither so constant nor so striking. The effects of urea feeding on allantoin excretion were similar to those produced by the feeding of amino acids." The results are so completely at variance with the studies on endogenous purine metabolism in man following the ingestion of protein and amino acids in excessive amts. that their explanation is difficult and further expts. are in progress which it is hoped will throw further light on the comparative endogenous purine metabolism.

A. P. LOTHROP

**Studies on yeast. VII. The dietary properties of yeast.** V. E. NELSON, V. G. HELLER AND E. I. FULMER. *J. Biol. Chem.* 57, 415-24 (1923); *cf. C. A.* 17, 2304.

Yeast is a rich source of vitamin B, not only for growth but for reproduction, as 3rd generation animals have been reared on 5% of yeast as the sole source of vitamin B. The postulation of a new vitamin for reproduction as suggested by Evans and Bishop (*C. A.* 17, 1045) is unnecessary. The majority of the young are not reared on synthetic diets contg. yeast as the only source of vitamin B but this failure is not due to any substance of a toxic nature in yeast. Yeast proteins furnish all the amino acids necessary for growth and 3rd generation animals were obtained on diets contg. 45, 40, 35, and 30% of yeast as the sole source of protein. With 25% of yeast the young grow far below the normal rate. To make the ash constituents of yeast complete Ca, Na, and Cl only need be added.

A. P. LOTHROP

**Vitamins in mollusks. Presence of an antiscorbutic factor in the oyster.** MME. RANDOIN. *Compt. rend.* 177, 498-500 (1923).—Four lots of guinea pigs were fed a diet which was complete except for the absence of vitamin C. The first lot received no addn. to this diet, the second lot received daily 3 cc. of citron juice, the third lot 16 g. of hashed fresh oysters, and the fourth lot both 3 cc. of citron juice and 15 g. of oysters. Animals in the first lot died in 28 to 33 days with scurvy. Those in the remaining 3 lots were healthy and increased in wt. After feeding the oysters for about 12 days to one of the



guinea pigs, during which time there was a gain of about 50 g. in wt., the oysters were withheld from the ration for about 6 days, during which time there was a steady fall of about 70 g. in wt. The fall in wt. immediately ceased and was followed by a rise on restoring oysters to the ration.

L. W. RIGGS

#### ABNORMAL

**A study of several cases of cystinuria.** J. M. LOONEY, HILDING BERGLUND AND R. C. GRAVES. *J. Biol. Chem.* 57, 515-31(1923).—The subjects included an individual from whose kidney a pure cystine stone had been removed, her two sisters, and her two sons and a man who served as the subject for the investigation of Alsberg and Folin 17 years ago. In the last case there had been practically no change in the condition of the patient during the intervening time with respect to his cystine metabolism. "The excretion of cystine is not simply an index of a general disturbance in the metabolism of the amino acids but a definite entity confined to cystine. The cystine S accounts for practically all the neutral S found in cystinuria provided the patient has not been taking  $\text{NaHCO}_3$  or cinchophen. The administration of  $\text{NaHCO}_3$  causes a marked disturbance in the distribution of neutral S owing to the decrease in cystine eliminated. This disturbance is not confined solely to the metabolism of cystine as the other amino acids are also affected, but in the reverse direction. No explanation is attempted for the remarkable changes caused by the  $\text{NaHCO}_3$  but it is hoped that further work will clear up the situation. The total amt. of cystine excreted depends on two factors: a relatively small but const. amt. derived from the endogenous metabolism and a large fraction which varies in proportion to the protein intake. When cystine is fed as the isolated amino acid only a very small amt. is excreted unchanged; there seems no reason to believe, therefore, that pure cystine is not utilized by the cystinuric individual." The element of infection does not seem to be an important factor in the formation of cystine stones and the subject is surrounded with the same obscurity which cloaks the problem of urinary calculi in general. Clinicians should insist that all stones be analyzed for the diagnosis of the disease may depend upon such an analysis. A. P. LOTHROP

**Clinical calorimetry. XXXIII. The effect of fasting in diabetes as compared with a diet designed to replace the foodstuffs oxidized during a fast.** H. B. RICHARDSON AND E. H. MASON. *J. Biol. Chem.* 57, 587-611(1923).—The quantity of protein, fat, and carbohydrate oxidized by 7 diabetic patients while fasting was detd. by means of the respiration calorimeter. The same amts. were then given in the diet (replacement diet) and the effect of fasting as opposed to this diet was observed. The total metabolism and the amts. of protein, fat and carbohydrate oxidized were used as a basis for comparison. The metabolism rose with the replacement diet only slightly above the basal level, on the av. 2.6%, so that this diet seemed to hold the metabolism at the level previously reached by fasting. The ingestion of the replacement diet was attended by an increase in the amt. of protein and carbohydrate oxidized and in the amt. of glucose excreted. To remedy this defect the allowance of protein and carbohydrate should be curtailed and the fat correspondingly increased, thus approaching the Newburgh and Marsh type of diet (*C. A.* 15, 551). When the subjects received their basal caloric requirements plus considerable amts. of fat in several instances, they oxidized more protein and carbohydrate and less fat than they received; in other words to their allowance of food they added protein and carbohydrate derived from their own tissues and subtracted a considerable portion of fat for storage. The tissues of undernourished diabetics seem to soak up fat like a sponge; one patient who was emaciated to the last degree stored the entire amt. given and oxidized protein and carbohydrate instead. The amts. of food eaten by diabetics may be widely different from the quantities oxidized and calcs. based on the diet are subject to error. The patients were kept under close observation at rest and the results obtained apply strictly only to diabetics in the resting condition.

A. P. LOTHROP

#### F—PHYSIOLOGY

ANDREW HUNTER

**Metabolism and temperature.** HERMANN FREUND. *Naturwissenschaften* 11, 787-92(1923).—A review and discussion with a bibliography. C. C. DAVIS

**Study of the colostrum with special reference to the effect of heat (pasteurization) on its physico-chemical, bacteriological, immunological and nutritional changes.** A. C. RAGSDALE AND S. BRODY. *Missouri Agr. Expt. Sta., Bull.* 197, 49-50(1922).—Out of 23 calves fed for the 1st 3 days after birth on colostrum pasteurized at 140° F. for 30 min., 2 died after 4 days; but the remaining 91.3% were successfully raised. The amboceptor of infectious abortion was not affected by heating colostrum to 149° for 1 hr. The time required to coagulate colostrum ranged from 14 hr. at 135.5° F. to 45-50 sec.

at 167° F.; at 140°, where the time required to inactivate the tuberculosis organism was 20 min., the time for coagulation of colostrum was 3 hr.; at 144.5° F. the times were 18.5 and 30–40 min.; at 149° F., 14 and 10–15 min.; and at 158° F., 3 and 2 min., resp.

P. R. DAWSON.

**Cerebrospinal fluid. III. Relation between the ventricular and the subarachnoidal fluid.** L. STERN AND R. GAUTIER. *Arch. intern. physiol.* 20, 403–36 (1923); *Physiol. Abstracts* 8, 178; cf. *C. A.* 16, 951.—All substances contained in or introduced into the ventricular fluid pass into the subarachnoidal fluid. Passage of a substance from the subarachnoidal into the ventricular fluid is not invariable, and occurs only when the pressure in the subarachnoidal spaces exceeds a definite value. Substances introduced into the ventricular fluid may be recovered from the deeper portions of the nerve tissues. Substances introduced into the subarachnoidal fluid can be recovered from the nerve tissues only when they can be detected in the ventricular fluid. The course of the cerebrospinal fluid by diffusion apparently is from the ventricles into the subarachnoidal spaces, then into the blood. The most certain method of reaching the nerve elements is the introduction of a given substance directly into the ventricular system.

JOSEPH S. HEPBURN.

**Uric acid in the bile. III.** THEODOR BRUGSCH AND JULIUS ROTHIER. *Klin. Wochschr.* 2, 1209–10 (1923).—The bile collected from the gall bladders of corpses was dild. with 10 vols. of H<sub>2</sub>O, treated with 1.6 cc. of 95% H<sub>2</sub>SO<sub>4</sub> per 100 cc. of liquid and boiled for 3 hrs. The mixt. was neutralized with NaOH, then acidified with HIOAc, made up to vol. and a Cu pptn. conducted on an aliquot part of the clear supernatant liquid. The pptd. Cu salt was freed from Cu with H<sub>2</sub>S in H<sub>2</sub>O soln., and uric acid obtained in crystals from the Cu-free liquid. The uric acid was detd. gravimetrically or colorimetrically, depending upon the quantity that was present. The following amts. of uric acid were found to be present in 11 cases: 100 cc. of bladder bile contained 10.71, a trace, 3.3, 5.05, 39.96, 23.1, 10.98, 24.7, 10.6, 34.96, and 49.81 mg. resp. The bile is of importance as a medium for excreting uric acid. Cf. *C. A.* 17, 306.

MILTON HANKE.

**Organs of internal secretion during human embryonal and fetal life. I. The thyroid.** F. LIVINI. *Arch. ital. anat. embriol.* 18, 522–47 (1922); *Physiol. Abstracts* 8, 184 (1923).—The secretion in the thyroid of embryos of 35 to 52 mm. differs both morphologically and microchemically from the true colloid which first appears in embryos of 62 to 66 mm.

JOSEPH S. HEPBURN.

**Action of lymph-gland extracts upon the morphology of the blood.** GELEKA. *Giorn. clin. med.* 3, 1–4 (1922); *Physiol. Abstracts* 8, 48 (1923).—An ext. of finely divided calf lymph gland was prepd. with warm saline soln., filtered, and sterilized. Injection of 5 cc. of this ext. produced no change in the blood with respect to hemoglobin, erythrocytes, eosinophils, and basophils; the leucocyte count increased in 4 hrs. and returned to normal after 48 hrs.; the lymphocytes decreased after 48 hrs. and returned to normal after 72 hrs.; the large mononuclears showed a slight increase.

JOSEPH S. HEPBURN.

**Comparative study of the concentration of various anions and cations in cerebrospinal fluid and serum.** J. B. PINCUS AND BENJAMIN KRAMER. *J. Biol. Chem.* 57, 463–70 (1923).—The av. concn. of the anions and cations in normal serum and spinal fluid, expressed in mg. per 100 cc. of material, is as follows, resp.: Ca 9.6, 4.8; P 2.9 (adults) 4.6 (children), 1.3; NaCl 578, 712; K 20.9, 14.7; Na 328, 351; and CO<sub>2</sub> 55.6, 55.7 expressed in cc. of CO<sub>2</sub> per 100 cc. at 0° and 760 mm. of Hg. If the concn. is expressed in g. mols. per l., when the figures for the concns. of the oppositely charged ions in each fluid are multiplied by each other, the results are approx. the same for both the serum and cerebrospinal fluid. The equil. existing between the serum and spinal fluid is similar to that between serum and serous effusions as found by Loeb, Atchley and Palmer (*C. A.* 16, 2550). A study of the equil. suggests that the Donnan membrane equil. plays an important part.

A. P. LOTHROP.

**Studies in the physiology of muscular exercise. V. Oxygen relationships in the arterial blood.** H. E. HINWICH AND D. P. BARR. *J. Biol. Chem.* 57, 363–78 (1923); cf. *C. A.* 17, 2446, 2599.—“In 20 expts. on normal men at sea-level, doing short periods of vigorous work on a bicycle ergometer, O<sub>2</sub> content rose above the resting value during and after exercise. In 7 expts., both O<sub>2</sub> capacity and O<sub>2</sub> content were detd. There was a rise in both after exertion but the content was increased more than the capacity, indicating a greater degree of O<sub>2</sub> satn. in the arterial blood. Since both the O<sub>2</sub> content and satn. of hemoglobin are higher after vigorous exercise, no part of the hyperpnea from exertion in these expts. can be attributed to an anoxemia in the arterial blood. In 2 expts. the effect of more fatiguing exertion was observed. In one there was a slight rise in content in blood drawn during the 5th min. after exercise. In the other,

the content was the same in the 2nd min. after exercise as before. The capacity rose as usual so that the satn. of hemoglobin, and presumably the  $O_2$  tension, decreased. In exhausting exercise it is possible that an anoxemia in the arterial blood may play a part in the causation of hyperpnea. The conflicting results in the literature may be explained by the following hypothesis: During exercise, arterial content is chiefly detd. by the opposing effects of  $O_2$  diffusion in the lungs and the velocity of the blood stream. In the normal man, arterial content may go through two stages if the exertion is severe. Early in exercise diffusion improves more rapidly than the circulation rate, and arterial content rises. Later, diffusion increases slowly, so that the continued rise in circulation rate reduces arterial content. It is possible that the severity of the exercise which a normal individual will tolerate may be detd. by the amt. of  $O_2$  which can diffuse through the lung membrane rather than by the capabilities of the circulation."

A. P. LOTHROP

**Experimental studies concerning the site of origin of bilirubin.** A. R. RICH. *Bull. Johns Hopkins Hosp.* 34, 321-9(1923).—Hemoglobin introduced into the blood stream of a dog without a liver and circulating actively as long as  $5\frac{1}{2}$  hrs. is not transformed into bilirubin. Since, however, the production of bilirubin from circulating hemoglobin takes place rapidly and readily in a dog with a liver through which the blood stream passes, it is concluded that the liver is necessary for the transformation of circulating hemoglobin into bilirubin. The conclusions are applicable only to hemoglobin circulating in the blood stream, not to hemoglobin liberated into the tissues from extravasated blood; the conversion of hemorrhage hemoglobin into bilirubin (hematoidin) is a purely local phenomenon, the exact mechanism of which still remains a question for study.

A. P. LOTHROP

**The normal variations in plasma hydrogen-ion concentration.** G. E. CULLEN AND H. W. ROBINSON. *J. Biol. Chem.* 57, 533-40(1923).—Data are presented on the variation of the plasma  $p_H$  in 27 normal medical students together with parallel observations on the alkali reserve and  $O_2$  contents and capacities in large proportions of the samples. The  $p_H$  of the plasma varied from 7.28 to 7.41 and lay between 7.35 and 7.40 in 21 out of the 27 specimens. However it is evident that any  $p_H$  values, measured at  $38^\circ$ , between 7.3 and 7.4 must be accepted as normal and it is probable that in a similar no. of normals taken at random there would be greater variations than in this group where all conditions were so uniform. These facts would lend support to the view that the ordinary normal individual and day by day variations in the reaction of the blood are greater than has been supposed. Within the normal limits of  $p_H$  and  $CO_2$  content there is apparently no systematic relation between the variables,  $p_H$  and  $CO_2$  content nor between  $CO_2$  and hemoglobin content. Variations between the  $pK_1$  (of Hasselbalch's equation) values of whole blood and plasma from 0.017 to 0.058 were observed so that it is evident that there exists, over the normal range, a rather large variation in the  $\Delta pK_1$  values.

A. P. LOTHROP

**Superventilation and carbon dioxide elimination.** J. T. KING, JR. AND VIRGINIA B. CROSS. *Bull. Johns Hopkins Hosp.* 34, 349-57(1923).—In the detn. of the basal metabolism by the  $CO_2$  elimination method two consecutive periods of observation should always be used, as it is a simple matter to recognize the effect of superventilation by the sharp drop in  $CO_2$  output in the 2nd period. If superventilation occurs, the test should be repeated on another day because of subsequent retention of  $CO_2$ . If there is any hesitancy in using the method for fear of the effects of superventilation, a comm. gas meter may be placed between the patient and the source of fresh air and an approx. estn. of the ventilation rate obtained therefrom. In a series of 200 consecutive detns. of the basal metabolism from  $CO_2$  elimination there was no elevation of the  $CO_2$  output that was not supported by clinical data. A comparison of the number of supernal metabolic rate detns. among patients not suspected of hyperthyroidism as shown by 3 methods is as follows: Tissot gasometer 12.7%, Benedict closed system 25.7%,  $CO_2$  elimination 2.4-7%. In the last method the % could not be raised above 7 by including all border-line cases of hyperthyroidism.

A. P. LOTHROP

**Study of the influence of chemicals on erythrocyte membranes by changes in corpuscular volume.** B. S. NEUHAUSEN AND J. E. BRESLIN. *Bull. Johns Hopkins Hosp.* 34, 199-201(1923).—The effects of the salts of the blood and of glucose on the erythrocyte membranes as shown by a comparison of cell vols. in iso-osmotic solns. were studied. The increase in corpuscular vol. was greatest in solns. of KCl; the least swelling was noted in the case of  $CaCl_2$  with only slightly more in NaCl and glucose. The ions increase the firmness of the membranes in the series  $Ca > Na > K$ , or from the point of causing swelling the series is  $Ca < Na < K$ . The contracting action of Ca on the corpuscles as opposed to the swelling action of K is another instance of the Ca-K

antagonism. "The expts. again emphasize that in the case of blood corpuscles we are not dealing with dead membranes such as  $K_2Fe(CN)_6$  which are only slightly affected by salt solns., but rather with very complex colloidal mixts., the swelling or ptosis of any component of which will loosen the whole structure." A. P. LOTHROP

#### G.—PATHOLOGY

H. GIDEON WELLS

**The etiology of acute intestinal intoxication in infants.** GLADYS L. BOYD. *Arch. Intern. Med.* 31, 297-301 (1923); cf. C. A. 17, 1666. —In the former abstract the journal reference was incorrect. E. J. C.

**Hydrogen-ion studies. VII. Experimental nephritis in rabbits with monobasic sodium phosphate.** E. F. HIRSCH. *Arch. Intern. Med.* 31, 862-5 (1923). The subcutaneous injection of 4 cc. 20%  $NaH_2PO_4$  per kg. body wt. on each of 2-4 days produced in rabbits a necrosis of the cells lining the convoluted tubules and loops of Henle. The pH of the blood was lowered to about 7.04 and the  $CO_2$  capacity to 12.28%. I. G.

**Metabolism in fever.** E. GRAPE. *Klin. Wochschr.* 2, 1005-9 (1923). —A review.

MILTON HANKE

**The fibrinogen concentration of the blood in hepatopathies.** K. ISAAC KRIEGER AND ANNA HIEGE. *Klin. Wochschr.* 2, 1067-9 (1923). —The fibrinogen content of the blood is reduced in cases of acute atrophy of the liver. Parenchymatous involvement of the liver often leads to a reduction in the fibrinogen content of the blood. The extent of the injury cannot be ascertained from the fibrinogen values; hence the prognostic and diagnostic value of the method is limited.

MILTON HANKE

**Blood regeneration in anemic mice in the dark, in sunlight, and under the influence of artificial ultra-violet light.** HANS ROBERT. *Klin. Wochschr.* 2, 1213-4 (1923). —The red blood count and hemoglobin value are reduced in normal white mice, when the mice are kept in the dark. Blood regeneration is very slow in acutely anemic mice that are kept in the dark. These mice frequently die. When exposed to daylight, the anemic mice recover completely within 13-14 days. A careful irradiation with ultra-violet light leads to a rapid regeneration of the erythrocytes in 10 to 11 days. The hemoglobin value rises more rapidly than the blood count. If the irradiation is too vigorous, blood cells are destroyed.

MILTON HANKE

**Non-specific reactions induced by proteins.** R. BIELING. *Klin. Wochschr.* 2, 1245-8 (1923). —A review with bibliography.

MILTON HANKE

**The occurrence in serum of a lipase foreign to blood.** H. PETOW AND H. SCHREIBER. *Klin. Wochschr.* 2, 1248-50 (1923). —For a description of the method and previous results see C. A. 17, 823. A quinine-stable, atoxyl-sensitive lipase, liver lipase, was found in the sera of all hepatopathies whose blood contained bile constituents. A similar quinine-stable lipase was found in the sera of patients having destructive nephritis. Kidney lipase does not appear in the serum in mild cases of nephritis. Since all organs contain lipase, it is possible that a marked destruction of the tissue of any organ may lead to the appearance, in the serum, of that organ's specific lipase. M. H.

**The nature of the crystals that occur in the sputum of asthmatics.** W. STORM VAN LEEUWEN AND D. R. NIJK. *Klin. Wochschr.* 2, 1268-9 (1923). —The Charcot-Leyden crystals, that frequently occur in the sputum of asthmatics, consist of  $CaHPO_4$ . The less frequently occurring rhombic crystals consist partially of  $CaHPO_4$  and partially of  $CaCO_3$ .

MILTON HANKE

**Titer vs. the fixability of complement.** R. L. KAHN AND E. D. WHITE. *Abstracts Bact.* 5, 17 (1921); cf. C. A. 16, 1807. —Apparent lack of fixing power by a good hemolytic complement may be due to the use of (1) an av. diln. of complement instead of a titrated number of units, or (2) a weakly positive serum, or (3) fixation at incubator temp. instead of ice box temp. for 4 hrs.

JOSEPH S. HEPBURN

**Cases of starvation edema in Italian ex-prisoners in Austria and Serbia.** G. FRACASSI. *Ann. d'ig.* 32, 371 (1922); *Physiol. Abstracts* 8, 48 (1923). —In starvation edema, the tissues, upon which the body is living, liberate toxins. These toxins then produce various changes in the viscera, chiefly fatal lesions of the kidneys and the liver.

JOSEPH S. HEPBURN

**Infantile scurvy.** J. C. GIDDINGS. *Arch. Pediatrics* 40, 508-18 (1923). —A review.

JOSEPH S. HEPBURN

**Mechanism of parasympathetic glucemia.** A. BORNSTEIN AND K. HOLM. *Biochem. Z.* 132, 138-53 (1922). —A decrease in the dextrose content of the blood follows extirpation of both suprarenals but does not produce death. The blood sugar varies within wide limits shortly before death, and increases at the moment of death in proportion to the glycogen content of the liver. Pilocarpine produces hyperglucemia.

in suprarenalectomized dogs to approx. one-half the extent it does in normal dogs; the hyperglucemia is not due to asphyxia; atropine does not abolish the CO glucemia in such exptl. animals.

JOSEPH S. HEPBURN

**Specific agglutination by antigens charged with normal antibodies.** G. H. BOISSEVAIN. *Compt. rend. soc. belge biol.* **2**, 165-7(1922); *Physiol. Abstracts* **8**, 83(1923).—Whenever an antigen (cell or bacterium) is charged with agglutinins of fresh serum, it acquires the property of agglutinating specifically additional quantities of the same antigen. However, chicken serum is an exception, for it imparts to ox cells the ability to agglutinate those of the dog as well as those of the ox.

JOSEPH S. HEPBURN

**Relationship between the agglutinins of fresh serum and the immuno-agglutinins.** G. H. BOISSEVAIN. *Compt. rend. soc. belge biol.* **2**, 167-9(1922); *Physiol. Abstracts* **8**, 83-4(1923).—A specific agglutinin is composed of a nucleus of antigen charged with normal agglutinins. Immuno-agglutinins have the same properties as antigens charged with normal antibodies (see preceding abstr.). Anti-ox chicken serum possesses the same properties as ox cells charged with fresh chicken serum.

JOSEPH S. HEPBURN

**Calcium and inorganic phosphorus content of the blood serum of the suckling.** P. GYRGY. *Jahrb. Kinderheilk.* **99**, 1(1922); *Physiol. Abstracts* **8**, 38(1923).—The ratio of Ca to phosphate is high in rickets and low in tetany. The phosphate and bicarbonate content of the blood, and the ionization of its Ca are also discussed.

JOSEPH S. HEPBURN

**Control of the lipase content of the blood.** E. BACH. *Z. klin. Med.* **95**, 103-8(1922); *Physiol. Abstracts* **8**, 39(1923).—The lipase content of the serum is not influenced by the diet, even when the latter is rich in fat. Lipase is inhibited by atoxyl *in vivo*.

JOSEPH S. HEPBURN

**The gas exchange in diseases of the thyroid gland.** J. T. KING, JR. *Bull. Johns Hopkins Hosp.* **34**, 304-11(1923).—"CO<sub>2</sub> elimination affords the best index to the heat production in thyroid disease as judged by direct calorimeter expts. Indirect calorimetry by the chamber method is a trifle less accurate than CO<sub>2</sub> as an index to direct calorimetry. This is doubtless the effect of the O<sub>2</sub> figures in the calcn. of cals., or due to inaccuracies in the direct heat measurement. Bearing in mind the technical errors inherent in metabolism expts. by the direct method, the good correlation of CO<sub>2</sub> elimination with direct calorimetry shows that CO<sub>2</sub> is a fair index to heat production in hyperthyroidism and that the value of CO<sub>2</sub> as an index to heat production is not significantly altered by the slight reduction of the respiratory quotient in hyperthyroidism."

A. P. LOTHROP

**Observations on dogs with experimental pyloric obstruction. The acid-base equilibrium, chlorides, non-protein nitrogen, and urea of the blood.** A. R. FELTY AND H. A. MURRAY, JR. *J. Biol. Chem.* **57**, 573-85(1923); cf. *C. A.* **15**, 2493.—"In 7 dogs in which complete or partial pyloric stenosis was effected the following changes occurred after operation: a rise in  $p_H$  which, however, was only marked in 3 dogs that developed tetany but where it was of sufficient magnitude to make it seem highly probable that there is a causal relationship between diminished acidity and nerve hyperirritability; a marked increase in BHCO<sub>3</sub> concn.; a very rapid diminution of chlorides in the plasma, whole blood and tissues which could be accounted for by the amt. of chloride secretion into the gastrointestinal tract above the point of obstruction; an inconsistent but in some cases a marked rise in urea and non-protein N of whole blood which necessitates further studies on N metabolism and the effect of alkalis on renal function to make it clear why there is an increase of the N waste products." In 2 dogs there was an increased concn. of the phosphates of the plasma and in 4 animals an increased elec. resistance was noted while taking electrocardiograms which were, however, entirely normal in form and wave interval.

A. P. LOTHROP

**The complement-fixation test in tuberculosis.** H. L. COULTHARD. *J. Path. Bact.* **26**, 350-79(1923).—By testing the actual amt. of complement which is fixed by mixts. of antigen and tuberculous serum, it was found that suspensions of killed tubercle bacilli in saline soln. are reliable and sensitive antigens; in general they give the most marked reactions. Next in value comes the alc. ext. from cultures of bacilli which have been previously treated with acetone. Stronger fixations are often obtained with this lipid antigen than with saline suspensions, but some tuberculous sera fail to fix complement in the presence of the lipid ext. The reaction is highly specific. It is independent of the Wassermann reaction and of the presence of heterophile antibody. It has little value for diagnosis in early or very active cases. Tuberculin in ordinary doses has no effect on the reaction.

JOHN T. MYERS

## H—PHARMACOLOGY

ALFRED H. RICHARDS

**Pharmacology of water.** H. C. HAMILTON. *J. Am. Water Works Assoc.* 10, 773-7; *Eng. News-Record* 90, 1128-9(1923).—The action of water on the human organism is one which increases secretion and improves digestion. Few substances, other than pathogenic organisms, render water unfit to drink, and most benefits derived depend on the quantity of water consumed rather than on any mineral peculiarities.

D. K. FRENCH

**Glucokinin.** II. J. B. COLLIP. *J. Biol. Chem.* 57, 65-78(1923); cf. C. A. 17, 2715.—From various plant tissues, by a variety of means, it was possible to obtain exts. which when subcutaneously injected into rabbits lowered the concn. of sugar in the blood. This effect did not occur promptly and, sometimes, not until several weeks had elapsed. In at least 1 instance, the moribund condition of the animal was relieved by the intravenous injection of glucose. Serum obtained from an animal made hypoglycemic with such exts. produced a similar effect when injected into another rabbit and this process could be repeated at least 5 times. A depancreatized dog was made aglycosuric by the injection of onion ext. (formation of abscess. Abstr.) and after subsequent reappearance of diabetic symptoms received another dose of onion ext. Ten days later the dog's urine was free from sugar and 2 days thereafter the dog died. Serum obtained from the heart blood caused hypoglycemia in rabbits. I. GREENWALD

**The action of acid phosphate solutions in tetany.** II. ELIAS AND F. KORNFIELD. *Klin. Wochenschr.* 2, 1206-9(1923); cf. C. A. 16, 4274.—The intravenous administration of 15 g. of either  $\text{Na}_2\text{HPO}_4$  or  $\text{NaH}_2\text{PO}_4$  leads to an increased elec. excitability and, after 2 hrs. to an attack of tetany in patients who had been free from attacks for some time. That the action was due to the phosphate ion and not to the salt concn., the reaction of the liquid or the Na ion was proved by suitable control expts. MILTON HANKE

**Injection of lactic acid and bilateral-vagotomy: a contribution to the peripheral chemical regulation of respiration.** A. PIRAS. *Arch. f. physiol.* 20, 359-67(1922); *Physiol. Abstracts* 8, 172(1923).—The sensitivity of exptl. animals to an increased H-ion concn., produced by intravenous administration of lactic acid, either remains unchanged or else is increased after the severance of both vagi. JOSEPH S. HENBURN

**Review of the use of insulin in the treatment of diabetes.** D. B. JEWETT. *J. Am. Inst. Homoeopathy* 16, 224-31(1923).—Insulin should not be used when the patient can be maintained in strength with sugar free urine and approx. normal blood sugar by dietetic methods. It should be used in diabetic coma, on diabetics before and after operations, and upon patients in whom the requisite diet produces glucosuria, hyperglycemia, and acidosis. JOSEPH S. HENBURN

**Quantitative studies with arsphenamine.** II. Distribution and excretion after intravenous injection. A. J. KOLLS AND J. B. YOUNG. *Bull. Johns Hopkins Hosp.* 34, 181-4(1923); cf. C. A. 17, 2433.—Approx.  $\frac{1}{4}$  of the injected arsphenamine leaves the blood stream within a few mins. after completion of the injection. The remainder is rapidly reduced in amt. but traces may be found after 24 hrs. The drug is stored in liver, spleen, kidneys, lungs, cardiac and skeletal muscle but alteration or excretion appreciably reduces the amt. after 3 hrs. The liver is a more important excretory organ than the kidney for arsphenamine and neoarsphenamine. The concn. of the drug in the brain is much lower than in any other tissue and, if the cerebrospinal fluid contains the drug at all, the amt. is too low to est. with accuracy. A. P. LOTHROP

**The effect of insulin treatment on the hydrogen-ion concentration and alkali reserve of the blood in diabetic acidosis.** G. E. CULLEN AND LEON JONAS. *J. Biol. Chem.* 57, 541-52(1923).—"The acidosis of severe diabetes is characterized by the lowering of both alkali reserve and plasma  $p_H$ . Under insulin treatment both alkali reserve and  $p_H$  return to their normal level coincidentally. There appears to be a consistent relation between these two factors during the return to normal. Two cases of coma with recovery under insulin treatment with plasma  $p_H$  at  $38^\circ$  of 6.98 and 7.02, resp., are reported. These are believed to be the lowest values for human plasma  $p_H$  with recovery that have been reported. That such abnormally low reactions are not in themselves incompatible with recovery is thus demonstrated." A. P. LOTHROP

**The bacteriostatic action of urine after the intravenous administration of mercurochrome to normal rabbits.** J. H. HULL AND J. A. C. COLSTON. *Bull. Johns Hopkins Hosp.* 34, 220-2(1923); cf. C. A. 14, 3470.—Inhibitive action of urine on bacterial growth following intravenous injection of 1, 2.5, 5 and 10 mg. of mercurochrome per kg. of body wt. into rabbits has been obtained. Bactericidal urine was obtained after a single injection of 1 mg. per kg. of body wt. in one case and after a single injection of 5 mg. in a 2nd case. Ten mg. per kg. of body wt. is about the lethal dose and causes a

violent diarrhea; with moderate doses the elimination is chiefly through the kidneys. The clinical trial of moderate intravenous doses is justified from the point of view of bacteriostatic action in *B. coli* infections of the urinary tract. A. P. LOTHROP.

The treatment of active infantile tetany with radiations from the mercury vapor quartz lamp. HORTON CASPARIS AND BENJAMIN KRAMER. *Bull. Johns Hopkins Hosp.* 34, 219-20 (1923).—In 5 consecutive cases of infantile tetany the symptoms disappeared after raying with the Hg vapor quartz lamp. In every instance the Ca concn. of the serum was increased by the treatment and the concn. of inorg. P was raised to the normal level or above. Not only did the manifestations of tetany disappear but healing of the rachitic process was effected. A. P. LOTHROP.

Studies of diabetes mellitus. III. The use of the pancreatic extract insulin in the treatment of diabetes mellitus. WM. S. McCANN, R. R. HANNON AND KATHERINE DODD. *Bull. Johns Hopkins Hosp.* 34, 205-19 (1923); cf. *C. A.* 17, 3700.—"Of 10 representative cases of severe diabetes treated with insulin, 9 derived some benefit, which was measured objectively in terms of lowered blood sugar values, decreased glucosuria, improved oxidation of glucose, and in control of ketosis, as well as in the relief of symptoms. Wide variations were observed in responses of the different patients to unit doses of the drug. The extra calcs. of food which patients were enabled to utilize per unit of insulin varied from 12 to 70 calcs. The amt. of extra carbohydrate which was utilized per unit (all sources of glucose being considered) varied from 0.5 to 3.6 g. In the presence of severe infections the action of the drug is apparently less effective." Exact diet regulation and cautious gradual balancing of the diet and dose are of great importance. For the relief of the symptoms of hypoglycemia due to overdosing orange juice is recommended but cane sugar is more convenient; the patient should always keep at hand a small amt. of carbohydrate in case of need. The use of adrenaline to counteract an overdose of insulin is not recommended as it is unreliable and produces other undesirable effects. A. P. LOTHROP.

The pharmacology of pyrethrum flowers. W. H. ZEIGLER. *J. Am. Pharm. Assoc.* 12, 19-26 (1923).—Six com. specimens gave from 3.81 to 6.85% of Et<sub>2</sub>O ext. A specimen of Dalmatian drug yielded 13% to H<sub>2</sub>O, 28 to EtOH, 2.8 to C<sub>6</sub>H<sub>6</sub>, 7.34 to acetone, 3.8 to Et<sub>2</sub>O, and 5.1% to CHCl<sub>3</sub>. The H<sub>2</sub>O ext. was inert. For the tests an ext. was prepd. by percolation with Et<sub>2</sub>O and spontaneous evapn. of the solvent. Mixed with sirup ants ate the ext. and died. It is highly toxic to the boll-woevil either by spray or in food. The ext. was dissolved in NaOH soln. contg. 0.4% NaCl and injected into the abdominal lymph sac of the grass frog, *Rana pipiens*. Stimulation, increased secretions, intermittent convulsions and death resulted. The substance placed in the stomach by a pipet produced the same effect but more slowly. By injections into the skin of the neck, turtles died with about the same symptoms as the frogs. The action lies in the spinal cord. Guinea pigs showed no toxic symptoms by subcutaneous injection of the ext. or by application of the powd. drug to the mouth and nostrils. The effects on rabbits by intravenous injection were variable; some of the animals died in convulsions. Blood pressure rose and then fell. The respiration was quickened and then depressed. Subcutaneous injections in the dog produced no effect; feeding the ext. in capsules gave no results; but intravenous injections produced convulsions which sometimes resulted in death. The convulsant dose of the ext. for dogs is about 40 mg. per kg. The convulsions are controlled by Et<sub>2</sub>O. L. E. WARREN.

A digitalis substance which is eliminated rapidly after its intravenous injection in the cat (WEISS, HATCHER) 17.

# I—ZOÖLOGY

R. A. CORTNER

Excretion of nitrogenous compounds by the frog at different temperatures. ST. J. PRZYŁECKI, J. OPIENSKA AND H. GIEDROYC. *Arch. intern. physiol.* 20, 207-12 (1922); *Physiol. Abstracts* 8, 44 (1923).—Increase in temp. produced a marked increase in the excretion of nitrogenous compds. by the kidney and a less marked increase in their excretion by the skin. JOSEPH S. HEFBURN.

Biochemical processes of fecundation. Lytic action of the perivitellin liquid of the eggs of teleosts. E. REMOTTI. *Arch. intern. physiol.* 20, 371-5 (1923); *Physiol. Abstracts* 8, 76.—During development, a protease appears in the perivitellin liquid of fertilized eggs of teleosts; it attacks the capsule of the egg and renders possible the exit of the mature larva. It is probably produced by a reaction between the protoplasm of the egg and the spermatozoa, and exerts an injurious action upon the latter. JOSEPH S. HEFBURN.

Asteriasterol—a new sterol from the starfish and the sterols of certain other ma-

**rine echinoderms.** I. H. PAGE. *J. Biol. Chem.* **57**, 471-7 (1923).—A new sterol, asterasterol, has been obtained from the eggs and body of the starfish, *Asterias forbesi*; m. p.  $\approx 70^\circ$ , of the acetate  $97^\circ$ , of the benzoate  $125^\circ$ , with the Liebermann-Burchard reaction an intense purple-blue color appeared immediately on the addn. of  $\text{H}_2\text{SO}_4$ , but the color disappeared almost entirely within 5 min.; Whitby's reactions (C. A. **17**, 1974) were atypical and represent a distinct advance in the means whereby sterol isomers may be differentiated. The sterols of the sand dollar, *Echinarachnius parma*, and of the sea urchin, *Arbacia punctulata*, are identical with true cholesterol. The sterols of *Cumia illinoensis*, *Choclopterus pergamentaceus*, and *Arenicola cristata* are probably identical with true cholesterol. The  $\text{AsCl}_3$  reaction is equally striking for oxysterol as for cholesterol; oxysterol dissolves in  $\text{AsCl}_3$  producing a deep violet which on gentle heating turns bright blue and on vigorous boiling bright green, the color changes being remarkably sharp and brilliant.

A. P. LOTHROP

## 12 FOODS

W. D. BIGELOW AND A. E. STEVENSON

**Some notes on butter analysis.** W. T. ROWE. *Chem. Eng. Mining Rev.* **15**, 450-2 (1923).—R. discusses the situation in South Australia arising out of the revoking in 1915 of the standard in force for butter. The discussion centers principally around the sol. and insol. volatile acids, for which R. recommends the Reichert-Messl-Wolny-Lefmann-Beam method for use in a standard method of analysis that he would like to see adopted and made official by South Australia.

E. G. R. ARDAGH

**Proposed butter-fat standard.** H. C. LYTHGON. *Chem. Age (N. Y.)* **30**, 463-4 (1922).—Out of 345 samples of butter examined, during 1920-22, 53.4% were below 82.5% fat but only 17.2% were below 80.0%. It is recommended that 80% fat in butter be the standard instead of 82.5%, as at present by Mass. law.

L. W. RIGGS

**Factors affecting the normal composition of milk factors influencing the percentage and quantity of fat in the milk of cows on official test.** A. C. RAGSDALE, S. BRODY and C. W. TURNER. *Missouri Agr. Expt. Sta., Bull.* **197**, 53-7 (1922).—Expts. with one group of cows showed approx. 0.2% increase in fat content for  $10^\circ\text{F.}$  decrease in the environmental temp. between the observed limits of  $30^\circ$  and  $70^\circ\text{F.}$  Sponging with cold water at 2-hr. intervals during the day tended to increase the fat % and total fat in the night milking. Variations in the % of fat in successive portions of milk as drawn from the gland were as previously reported (C. A. **15**, 4032). Data compiled from a large no. of yearly records are presented, demonstrating the relation of stage of lactation and seasonal variations to fat content and vol. of milk.

P. R. DAWSON

**Relation of the growth of bacteria to the coagulation temperature of evaporated milk.** L. A. ROGERS, E. F. DYSHER and F. R. EVANS. *Abstracts Biol.* **5**, 7 (1921); cf. C. A. **16**, 3139.—No very definite relation exists between the H-ion concn. of raw milk and the coagulation temp. of evaporated milk prepd. from it. However, the coagulation temp. may be lowered without appreciable change in the H-ion concn. by the growth of liquefying bacteria, and the resulting action of rennin on the casein.

J. S. HEPBURN

**Determination of fat in cheese.** J. GROSSFELD. *Pharm. Weekblad* **60**, 1069-78 (1923).—Heat 10 g. of cheese in a flask with 10-15 cc. of concd.  $\text{HCl}$  until the proteins are dissolved, cool and add exactly 100 cc. of  $\text{C}_2\text{HCl}_3$  at a definite temp. ( $15-20^\circ$ ). Reflux 3-5 min., then cool. Transfer to a separatory funnel, avoiding loss by evapn. Allow to stand for some time, and draw off the lower layer, filtering if necessary. Take a 25-cc. aliquot at the original temp., distil off the solvent over a free flame, and dry the residue at  $105-110^\circ$  to const. wt. Calc. the total fat from the equation  $x = 92a/(23 - a)$ , where  $a$  is the wt. of dry residue and 0.92 the sp. gr. of butter fat. For more accurate detns. a correction may be made for evapn. of solvent, by detg. such loss when a known amt. of butter fat is put through the same treatment. The correction factor is then the wt. of fat taken  $\div$  wt. found. Detns. by this method agree closely with those by the Bondzynski-Ratzlaff method.

A. W. DOX

**The effect of each ingredient in the manufacture of ice cream.** W. H. E. REID and D. H. NELSON. *Missouri Agr. Expt. Sta., Bull.* **197**, 58-9 (1922); cf. C. A. **16**, 3517.—Increase in butter fat content is accompanied by a uniform increase in sp. gr., gradual increase in viscosity, and increase in time required for the mixt. to start freezing. No relation was demonstrated between fat content and f. p. or hardness. The most desirable flavor, body, texture, richness and appearance were obtained with mixts. contg. 10-12% of fat and such were most readily maintained in salable condition after 5 days storage. Increases in content of sugar, milk powder, and condensed and evaporated



milk caused greater depression of the f. p.; gelatin, gum tragacanth and India gum had no such effect.

**Chemistry of concentrated grape juices and their derivatives.** GARINO-CANINA. *Riv. ampelografia* 1, 65-75(1920); *Bull. Agr. Intelligence* 11, 785-6(1921).—Grape juice (red or white) is concd. by refrigeration with removal of approx. 25% of the water, then is further concd. by evapn. under reduced pressure at a temp. of 35° to 40° to a d. of approx. 1.3 at 15°. The resulting *sirup* has the grape aroma. By further concn. to a d. of 1.38 to 1.44, a "grape honey" is obtained, a solid mass contg. minute crystals of dextrose and levulose. *Ampeloplastin*, *ampelagalactin*, and *ampelohematin* are manufd. by addn. of egg yolk, milk, and blood, resp., to the sirup prior to its further concn. An *integral ext. of marc* is made by systematic extn. of the grape press cake with slightly sulfated water at 35° to 40°, and concn. of the ext. to the d. of the sirup. The *honey* from the Favorita grape has a d. of 1.4025 at 25°, and the following compn.: ext. 79.86%, reducing sugars 75.72% including dextrose 42.47% and levulose 33.05%, total acidity calcd. as tartaric 0.82%, total tartaric acid 0.54%, malic acid 0.79%, ash 1.10%, total P 0.085%, org. P 0.009%. Data are also given on the partition of N in the different products.

**The role of oxygen in food spoilage.** T. M. RECTOR. *Canning Age* 1923, 15-6 (October).—Chemical changes taking place in foods which in time make them unfit for consumption are principally due to O. Discussions of such changes in nuts, oils, butter, eggs, salad dressing, dried milk, catsup, fish and olives are given.

**Dark discoloration in canned peas.** A. W. BITTING. *Canning Age* 1923, 27, 29 (October).—Discoloration was caused in this cannery by contact of blanched peas with a copper hopper.

**Destructive distillation of lemon residue.** H. D. POORE. *Chem. Age* (N. Y.) 30, 433-4(1922).—The annual production of lemon residue in the production of citric acid in California amts. to perhaps 30,000 tons contg. total solids 16.17%, cellulose 2.73, citric acid 0.6, protein 1.56, pectin 1.95, pentosans 2.61, ash 0.82. Expts. to det. if this residue could be made a source of AcOH, MeOH, Me<sub>2</sub>CO, or other products, showed that the possible chemicals which might be reasonably obtained from one ton of wet residue were worth less than \$1. Under present conditions it is advised to dispose of this waste residue by burning.

**Bread dough.** W. A. DARRAH. U. S. 1,468,775, Sept. 25. Dough for bread (or cake or other bakery products) is prepd. with an excess of H<sub>2</sub>O, to insure thorough hydration, and the excess moisture is removed from the dough by evapn. The evapn. may be induced by forcing small streams of air through shredded portions of the dough. Dil. NH<sub>3</sub> soln. may be used in small amt. as an alk. dispersing medium to facilitate the dough prepn. and in case of this or similar alkaline treatment of the dough it may afterwards be neutralized by the use of CO<sub>2</sub> or HCl (which may be added to the air current used for treating the dough).

**Testing bread doughs.** M. CHOPIN. U. S. 1,468,900, Sept. 25. Flours are tested for their bread-making properties by mixing H<sub>2</sub>O with the sample of flour to form a homogeneous dough and a layer of this dough is then clamped between plates with suitable orifices and subjected to distension by the action of gas under pressure to det. the pressure under which a sample of standard size and thickness will rupture.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**The chemist and industry.** H. H. GRAY. *Chemistry & Industry* 42, 956-8(1923).

**The new patent act in Canada.** C. L. JENKS. *Ind. Eng. Chem.* 15, 1192-3(1923).

**Cost of patents in foreign countries.** D. B. KEYES. *Chem. Met. Eng.* 29, 722 (1923).

**Catalysis.** K. C. BAILEY. *Science Progress* 18, 56-65(1923).—A discussion of catalytic reactions and their industrial application.

**Electrical power for chemical plants.** HARTLAND SEYMOUR. *Chem. Trade J.* 73, 421-2(1923).—About when to buy and when to generate.

**Relation of the chemical and dyeing industries.** MAX MUSPRATT. *Chem. Age* (London) 9, 368(1923).—An address.

**How do you operate a column still?** F. H. RHOODES. *Chem. Met. Eng.* 28, 590 2 (1923).—The advantages are shown of the single condenser and dividing box over the more common reflux condenser and final condenser as means for controlling the reflux ratio in column distn. Variation in distn. rate does not change the reflux ratio. The reflux ratio is easily adjusted to any desired value. High boiling solns. are distd. as readily as low-boiling.

E. H. LESLIE

**Charts for estimating temperature distributions in heating or cooling solid shapes.** H. P. GURNEY AND J. LURIE. *Ind. Eng. Chem.* 15, 1170 2, 1923. A graphical method is given for expressing the rate of cooling or heating in such solid shapes as the sphere, cylinder and slab. The factors entering into the calcns. are (1) time, (2) thermal diffusivity, (3) distance from center, axis or midplane, (4) thermal cond., (5) thermal surface cond. (emissivity). The method is illustrated by graphing results obtained from measurements made in a (1) rubber slab, (2) steel ingot, (3) slab of glass. The curves are nearly straight lines on arithlog paper.

E. G. R. ARDAGH

**Drying. Industrial drying. The apparatus and how it works.** LUCIEN BECK. *Chem. Met. Eng.* 29, 626-31 (1923).—The general principles of drying with air are set forth. There is a limit to the speed at which any material can be dried. If this limiting speed is exceeded injury, such as checking, warping, cracking, etc., usually results. Suggestions are made to designers of driers. Heat insulation is discussed. Driers are classified and as an example data are given and calcns. made for a drier for coco fiber mats.

E. G. R. ARDAGH

**Procedure for the desiccation of air.** PAUL DUMANOIS. *Compt. rend.* 177, 339 40 (1923).—The storage of large quantities of abs. alc. requires that the air in contact with the alc. shall be free from moisture. A description is given of a system of valves, tubes and compartments with baffle plates by which dry air is kept in contact with alc.

L. W. RIGGS

**Fine screening equipment—its selection and operation.** F. S. CURTIS. *Chem. Met. Eng.* 29, 759 (1923).—Screening equipment must be adjustable. Specifications stated in fractions of an inch instead of in "mesh" become more definite and dependable. The use of a screen in closed circuit with grinding equipment increases the output without increasing the power requirement.

W. H. BOYNTON

**Unloading the centrifugal.** B. C. LECHLER. *Chem. Met. Eng.* 29, 760 (1923).—A mech. unloader must be easy of operation for light duty and of rugged construction with carefully balanced stresses for heavy duty. One type of unloader has a vertical post carrying for part of its length a rack attached to the curb top. Sliding on the post is a sleeve, moved by a hand wheel and pinion which carries the main arm of the plow. This kneeshaped steel casting which slides on the vertical post and swings about it carries a vertical bronze arm reaching into the curb and carrying at its lower end the scraper. Design of the arm and scraper limits closely the pressure of the scraper on the lining.

W. H. BOYNTON

**Health conditions among chemical workers, with respect to earnings.** F. M. PHILLIPS AND CERTRUDE A. SAGER. *Public Health Repts.* 38, 2320 2 (1923).

E. J. C.

**The dusted lung with special reference to the inhalation of silica dust and its relation to pulmonary tuberculosis.** B. S. NICHOLSON. *J. Ind. Hyg.* 5, 220 42 (1923).

E. J. C.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

**Preliminary examination of water samples.** W. D. COLLINS AND MARGARET D. FOSTER. *Ind. Eng. Chem.* 15, 1078-80 (1923).—Detn. of Cl and alkyl. by the usual methods, and SO<sub>2</sub> and Ca turbidimetrically, will save time in making mineral water analyses. The turbidimetric tests are made with vols. of 10 cc. The SO<sub>2</sub> is pptd. by adding 1 cc. of acid BaCl<sub>2</sub> (48 cc. MCl (sp. gr. 1.19) and 100 g. BaCl<sub>2</sub> 2H<sub>2</sub>O per l.). For Ca, 1 cc. of AcOH (equal parts of 99.5% acid and H<sub>2</sub>O) is added, the soln. shaken and 1 cc. of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> soln. (0.2 g. per cc.) is added. Comparisons with standards are made after 10 min. Hardness by the soap method is often useful. These methods do not have an av. error of more than 10%.

J. M. HOLDEN

**The determination of dissolved oxygen in the presence of iron salts.** A. M. REE, WELL AND W. U. GALLAHER. *Ind. Eng. Chem.* 15, 1186-8 (1923).—A review of the literature on the detn. of dissolved O is given. In the presence of Fe salts the modified Winkler method was shown to give erroneous results which cannot be corrected for

on the basis of the amt. of Fe present. The Letts and Blake modification of the Levy method gives results which check gasometric detns. in the presence of Fe salts and org. matter.

**Expressing results of water analysis.** C. P. HOOVER. *Eng. Contr.* **60**, 103-4 (1923).—At Columbus, O., the routine detns. made are total alky., phenolphthalein alky., caustic alky., incrustants, total hardness, Mg and Ca. A method of plotting is described.

**Absorption of atmospheric gases by water.** J. H. COSTE. *Analyst* **48**, 433-5 (1923).—A graph is given for dissolved O<sub>2</sub> and "atm" N consisting of a series of isothermal curves showing as ordinates the vol. of O at normal temp. and pressure in l. l. of H<sub>2</sub>O of any salinity.

**Effect of deaeration of natural waters on the carbonate equilibrium.** D. H. JACKSON AND J. R. McDERMET. *Ind. Eng. Chem.* **15**, 959-61 (1923).—All of the free CO<sub>2</sub> and about 35% of the bicarbonate CO<sub>2</sub> are removed by complete deaeration. CaCO<sub>3</sub> is pptd., MgH<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> not being decompd. Percentage bicarbonate removed varies directly with the original concn. pH values are changed from acid to alk., the change averaging pH 2.5.

**Ammoniacal liquor for softening water.** M. CHEVALET. *Soc. Tech. du Gaz; Gas J.* **163**, 735 (1923).—Water used for gas washing or feed water can be freed from its CaCO<sub>3</sub> by the addn. of ammoniacal liquor either to the cold water or to the feed water heater. In the latter case at a temp. of about 60°, the NH<sub>3</sub> can be regenerated and used repeatedly so the consumption is small. The process is cheap, simple of control, and offers the possibility of replacing soda ash in any process employing the latter.

**Rapid sand filtration plant operation.** W. D. HATFIELD. *Eng. Contr.* **60**, 74-6 (1923); *Can. Eng.* **44**, 539-40 (1923).—A simple description, non-technical. L. P.

**Double coagulation in water filtration.** F. E. SHEEHAN. *Eng. Contr.* **60**, 542-3 (1923).—Experiences at Portsmouth, O., are described with a plant serving 40,000 people, using Ohio River water. A saving in coagulant resulted, with better operating control and a better filtered water.

**More about chlorination.** ANDREW BALFOUR. *Trans. Royal Soc. Tropical Med. Hyg.* **16**, 332-5 (1922); *Pub. Health Eng. Abstracts* July 28, 1923.—Addition of 1% lime to a 20-25% NaCl soln. upon electrolysis gave a soln. which contained 2.5% available Cl and which remained stable for 12 months. Use of this method is advocated for sterilizing water supplies in India.

**Movement of B. coli in ground water with resulting pollution of well.** C. W. STILES AND H. R. CROHURST. *Eng. Contr.* **60**, 100-2 (1923).—Tests have shown movement of *B. coli* for 65 ft. in fine sand effective size 0.13 mm. Uranin spread 115 ft. Pollution took 187 days to travel in a thin sheet.

**A study of the effect of gentian violet on the viability of some water-borne bacteria.** ESTHER W. STEARN. *Am. J. Pub. Health* **13**, 567-70 (1923); *Pub. Health Eng. Abstr.* Oct. 13, 1923.—Gentian violet does not inhibit the vigorous growth of *B. coli* or other important lactose-fermenting water-borne bacteria.

**B. coli in water in relation to health.** W. H. FROST. *Nation's Health* **5**, 527, 557-8 (1923).—The presence of true *B. coli* in water demonstrates beyond reasonable doubt that the water is polluted with fecal matter but it does not prove the water to be infectious. Sanitary surveys are valuable indicators of the possibility of infection, but epidemiological evidence is needed to establish and measure the actual danger of a water supply.

**Construction and operation of Warren, Ohio, water filtration plant.** S. N. VANCE AND P. J. O'CONNOR. *Munic. County Eng.* **64**, 183-8 (1923).—The rapid filter plant has a capacity of 6 m. g. d. divided into 6 units. Provision is made for dry feed of alum and lime. Mahoning R. water is treated by 3½ hour coagulation. A lab. is provided.

**Chlorine production at Independence, Mo.** A. H. GALLAGHER. *Public Works* **54**, 336-7 (1923).—An electrolytic cell produced Cl for a period of 222 days at 4.81c per lb. of Cl, with current at 1.7c per kw.-hr. The operation is said to be simple and the result good.

**Features of new well water supply at Memphis, Tenn.** J. R. McCLINTOCK. *Munic. County Eng.* **64**, 47-51 (1923).—A well water development will serve 175,000 people with 18 m. g. d. of water contg. 110 p. p. m. free CO<sub>2</sub>. Air lift pumping is used, the air supply being metered. Coke aerator trays are supplied in series of 4 superimposed, followed by rapid sand filters.

**The Bloomington, Ind., water supply problem.** PAUL HANSEN. *Munic. County*

**Eng. 64, 95-100(1923).**—The history is given from the first supply to the present improvement. The geologic conditions which detd. the final selection of the site of the dam and reservoir are described. Owing to failure of early works a serious water shortage resulted.

**Filter plant operation at St. Louis.** E. E. WALL. *Eng. Contr.* **60, 550(1923)**; cf. *C. A.* **17, 166**.—During the yr. ending April 1, 1923, an av. of 112.3 m. g. d. were filtered at cost of \$4.01 per mil. gal. Washing of filters is at rate of 15 gal. per sq. ft. per min. 1.409% of water was used.

**Size of filter sands at Lima, Ohio.** E. E. SMITH, 2d. *Pub. Works* **54, 282-3** (1923); *Eng. Contr.* **60, 102-3(1923)**.—The size of the sand is given for six filter units, with data on the loss of head, length of wash, etc., for 1921. All the sand is less than 0.45 minimum effective size. The data indicate the importance of grading the sand, the finer sand requiring more wash water.

**Benton Harbor purification plant.** PEARSE, GREELEY & HANSEN. *Public Works* **54, 285-9(1923)**.—This 2 m. g. d. plant treats both river and well water carrying Fe. Arrangement is made for overdosing a part of the water but this has not proved advantageous. A Dorr thickener is used for preliminary sedimentation (1 hr.) followed by 8 hrs. in 2 basins. Return sludge from the Dorr Clarifier adds sedimentation.

**Effect of filtration on typhoid death rate at Columbus, Ohio.** C. B. HOOVER. *Eng. Contr.* **59, 1058(1923)**. See *C. A.* **17, 2623**.

**Charles (S. C.) water treatment notes.** J. R. GIBSON. *Public Works* **54, 281-5** (1923).—The use of  $\text{Ca(OH)}_2$  and NaOH for softening filtered water (hardness 20 to 25 p. p. m.) is described, the soda treatment requiring about 2 grains of 76% NaOH per gal. as against 14 grains  $\text{Ca(OH)}_2$ . The cost is increased \$16.00 per day for the 6 mil. gal.

**Water purification at Columbus.** C. P. HOOVER. *Public Works* **54, 305**; *Eng. Contr.* **59, 1035-6(1923)**.—See C. B. Hoover, *C. A.* **17, 2623**.

**Cleaning water mains in Manhattan, Kansas.** B. L. FURICH. *Public Works* **54, 281-2(1923)**.—The water has a hardness of 150 p. p. m., contg 7 to 10 p. p. m. Fe. 7.8 miles of pipe were cleaned at cost of 11.6 cents per ft. The cleaning machine was drawn through by cable.

**Expediting drying of sewage sludge.** J. R. DOWNS. *Public Works* **64, 213-5** (1923).—Expts. on use of alum in dewatering Imhoff sludge at Plainfield reduced the drying period to 1/3 or less time. About 150 lbs.  $\text{Al}_2(\text{SO}_4)_3$  are used per 110 cu. yd. sludge.

**Condensed manual of sewage works operation.** BURNS AND McDONNELL. *Munic. County Eng.* **64, 170-2(1923)**.—This covers the routine instructions for operating sewage works of various types.

**Curing a sick sewer system.** L. B. REYNOLDS. *Public Works* **54, 160-2(1923)**.—To clean up conditions of nuisance in creeks, the sewage was treated in 3 plants, and ejectors put in 3 systems of sewers besides. The details are given.

**British developments in activated sludge.** H. C. SHENTON. *The Surveyor*; *Eng. Contr.* **60, 79-81(1923)**.

**Activated sludge process.** EDWARD BARTOW. *Public Works* **54, 216-9(1923)**.—English and American practices in aeration both with air and mechanically are described. The processing of sludge is summarized at various cities.

**Mechanics of activated sludge.** J. A. COOMBS. *Can. Eng.* **45, 201-7(1923)**.

**Practical solution of the problem of dewatering activated sludge.** J. A. WILSON, W. R. COPELAND AND H. M. HEISIG. *Ind. Eng. Chem.* **15, 956-9(1923)**; cf. *C. A.* **16, 980**.—At Milwaukee the untreated sludge obtained in winter was almost unfilterable. Acidifying the sludge to  $p_H$  3.4 and heating to 160° F. were found to give filter efficiencies in winter equal to the best summer efficiency. Acidifying to  $p_H$  4.1, heating to 160° F., and adding 1 lb. of alum for every 50 gals. of sludge further increased the efficiency.

**Fine screening at activated sludge plant, Milwaukee.** ANON. *Eng. Contr.* **60, 576-7(1923)**.—This describes the Tark screens being built for Milwaukee.

**Sewage experimental work at Plainfield, N. J.** WILLEM RUBINUS. *Can. Eng.* **45, 329-31(1923)**; cf. *C. A.* **17, 3391**.—An investigation of the microscopic life in an Imhoff tank and a sprinkling filter was made. Gas analyses from an Imhoff tank showed  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$ . The biol. changes through a yearly cycle in the filter are quantitatively shown.

**Complete sewage treatment for city of 3000, Delaware, Wis.** W. A. PIERCE.

*Munic. County Eng.* **64**, 92-3(1923).—A small plant, with modified Imhoff tank with upward flow through slots, followed by trickling filters, handles 75,000 gal. sewage per 24 hrs.

LANGDON PEARSE

**Rochester's Brighton sewage disposal plant.** J. F. SKINNER. *Public Works* **54**, 218(1923).—In 1922 the plant handled 9000 people, with 1 mil. gal. daily, the Imhoff tank removing 60% of the suspended solids. The effluent of the trickling filter is stable for 21 days.

LANGDON PEARSE

**Sewage treatment plant at Cochrane, Ont.** ANON. *Can. Eng.* **45**, 321-3(1923).—The activated sludge plant for 6000 population handles 500,000 imp. gal. per 24 hrs., and comprises 8 aerating tanks 9 ft. deep, with eccentric plates and hopper bottom settling tanks with 60° slopes. The entire plant is covered. The aerating tanks are arranged around the settling tanks.

LANGDON PEARSE

**Operation of the Gloversville sewage disposal plant.** H. J. HAMMER. *Public Works* **54**, 199-200(1923).—In a city where 35-40% of the sewage is tannery waste the flow treated in 1922 avd. 2.94 m. g. d., with 3.4 ft.<sup>3</sup> of screenings per mil. gal. and 1.04 ft.<sup>3</sup> of grit. 5935 gal. sludge were removed from primary Dortmund tanks per mil. gal. with a solid content of 4.44 and sp. gr. 1.015, or 1930 lbs. dry solid per mil. gal. Three acres of trickling filters are operated, 1 acre being rested for 2 weeks in turn. From the secondary tanks 2050 gal. of sludge per mil. gal. have been removed, with a per cent solids 6.02, sp. gr. 1.016 or 1030 lbs. per mil. gal. The 2.65 acre sludge bed produced 5677 yd.<sup>3</sup> dry sludge, from a depth applied of 9.4 ft.

LANGDON PEARSE

**Method of sewage disposal in the City of Brocton.** H. S. CROCKER. *Nation's Health* **5**, 515-6(1923).—Plain sedimentation and trickling filters are used in conjunction with a sand filtration plant.

J. M. HOLDERBY

**Beccari system of organic waste disposal.** ANON. *Nation's Health* **5**, 533-5(1923).—This system, an Italian development, provides for the disposal of org. wastes by fermentation in a closed cell so arranged as to conserve practically all of the liberated N. The system is regarded as a success in Italy and tests in this country, made at Paterson, N. J., indicate its success here. Org. wastes are dumped into a ventilated brick and mortar cell and are allowed to ferment for 30-40 days. *Advantages:* The cells are simple in construction; after filling no care is required until the process of fermentation is completed; the product is well digested, free from odor, and can be dumped without creating a nuisance. There are no odors around the plant, and the cost of upkeep is slight.

J. M. HOLDERBY

**Beccari system of garbage disposal.** ANON. *Public Works* **54**, 197-8(1923).—See preceding abst.

LANGDON PEARSE

**Treatment of laundry wastes.** F. E. DANIELS. *Public Works* **54**, 190-1(1923); *Public Health Eng. Abstr.* Sept. 8, 1923.—Alky. was corrected with H<sub>2</sub>SO<sub>4</sub> (pH 2.6 for lime or 7.0 for alum), followed by treatment with lime or alum, and after settling the clear supernatant liquor run off. The sludge is dried on beds. Instead of H<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub> may be used with lime but the detention period is increased. The cost of the acid alum treatment is the lowest.

G. C. BAKER

**Present status of sanitary engineering.** H. P. EDDY. *Eng. Contr.* **59**, 1053-8(1923).

LANGDON PEARSE

**Practical methods for the removal of dust and fumes.** H. H. VALIQUET. *Nation's Health* **5**, 519(1923).—Standard hood areas and air velocities are given. Recommendations are made for various special installations.

J. M. HOLDERBY

Value of sludge as fertilizer (HATTON) 15.

**Deoxidizing water with ferrous hydroxide.** R. G. KNOWLAND. U. S. 1,470,084, Oct. 9. H<sub>2</sub>O to be deoxidized is charged with Fe(OH)<sub>2</sub> in excess of the amt. required to absorb the free O in the H<sub>2</sub>O and while the deoxidized H<sub>2</sub>O is retained in a closed app. to prevent reabsorption of O it is filtered to remove the Fe(OH)<sub>2</sub> formed.

**Sterilizing water with chlorine.** W. PATERSON. U. S. 1,468,739, Sept. 25. In supplying Cl to H<sub>2</sub>O or other liquid to be treated, the flow of Cl is obstructed by a seal of H<sub>2</sub>SO<sub>4</sub> or other relatively inert liquid by the periodic displacement of which definite measured amts. of Cl are supplied.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**Efficiencies of phosphatic fertilizers as affected by liming and by the length of time the phosphates remained in Porto Rican soils.** P. L. GILF AND J. O. CARRERO. *J. Agr. Research* 25, 171-94(1923).—The relative efficiencies of phosphatic fertilizers vary widely in different soils. None of the 5 phosphates studied varied in efficiency directly with the CaO requirement of the soil although rock phosphate and bone meal were generally most efficient in soil with high CaO requirements. Applications of CaO equiv. to the CaO requirement decreased the efficiencies of the phosphates in most soils. Practically no difference in efficiency was observed regardless of whether the CaO was applied 6 weeks before or immediately before the phosphate was applied. A comparison of the efficiencies of phosphates applied 6 weeks before planting with that of phosphates applied immediately before planting showed that the former diminished very appreciably in all soils whether limed or not. Acid phosphate continued to lose in efficiency the longer it remained in the soil. That such losses are of general occurrence and that they are due to the action of soil constituents rendering the  $P_2O_5$  unavailable to the plant is indicated by the fact that as a rule only 10 to 20% of the  $P_2O_5$  applied is recovered in the crop, whereas 60 to 90% of the N or  $K_2O$  applied is commonly recovered.

W. H. ROSS

**Influence of some nitrogenous fertilizers on the development of chlorosis in rice.** L. G. WILLIS AND J. O. CARRERO. *J. Agr. Research* 24, 621-30(1923).—The greater tendency to the development of chlorosis in young rice plants following fertilization with nitrates as compared with  $NH_4$  salts may be based on the influence on the plants at the period of greatest absorption of N of the unassimilated residues of the fertilizer used rather than on the inferiority of nitric N as a nutrient. It is probable also that the N of  $Ca(NO_3)_2$  is suitable equally with that of  $(NH_4)_2SO_4$  in the physiological processes of the rice plant when it is used under cultural conditions in which the reaction of the unassimilated residue of the nitrate does not interfere with the absorption and utilization of Fe.

W. H. ROSS

**Experiment on the utilization of synthetic urea as a nitrogenous fertilizer.** GASTON CHEVALIER. *Prog. agr. vil.* 80, 257-60(1923).—Compared with equiv. amts. of N in the several corn forms, synthetic urea gave, in a pot expt. with spring wheat, results equaled only by  $NaNO_3$ , as demonstrated by rate of germination and growth.

P. R. DAWSON

**Tests of value of sludge as fertilizer.** T. C. HATTON. *Eng. Contr.* 60, 538(1923).—The results of tests at several points are cited where comparisons were made. The results varied.

LANGDON PEARSE

**Determination of the potash in cane juices as an indication of the fertilizer requirements of the soil.** H. WALKER AND G. B. GLICK. *Intern. Sugar J.* 25, 478-81(1923); cf. *C. A.* 17, 1161.—Former studies on P requirement of cane soils have been extended to K. To prep. the juices for the  $K_2O$  detn., make 500 cc. of juice of known sp. gr. slightly alk. to phenolphthalein with  $Ca(OH)_2$ , boil and filter through a Buchner funnel. Of the clear filtrate, conc. 150 cc. to less than 50 cc., and wash into a 50-cc. flask. Add 2.8 cc. glacial AcOH, cool to not less than 22°, and complete the vol. Det.  $K_2O$  by Sherrill's method (*C. A.* 15, 1114), using 5 cc. of the prepd. sample; the %  $K_2O = (50 \times \text{reading of sample}) \div (150 \times \text{sp. gr. of juice} \times \text{reading of standard soln. of } 1\% K_2O)$ . Cane juice samples from plots fertilized with K contained much more K on the av. than the checks. It appears that cane juice with less than 0.05%  $K_2O$  indicates need of K fertilizer, and 0.1% or more no such need.

W. J. OWEN

**Injury to foliage by arsenical spray mixtures.** D. B. SWINGLE, H. E. MORRIS AND EDMUND BURKE. *J. Agr. Research* 24, 501-37(1923).—The arsenical insecticides least injurious to foliage are Fe arsenate and certain of the Pharsenates. When promptly applied after mixing with water,  $As_2O_3$  is not as injurious to the foliage as is generally supposed, but standing after mixing causes a marked increase in injury. Of the readily sol. arsenical compds., cacodylic acid and Na and K cacodylates are the most injurious. Soap added to sol. arsenicals offers a slight protective action, but increases the injury caused by insol. arsenicals. Lime-S increases the injury caused by most insol. arsenicals but tobacco ext. has little influence on the injurious properties of such compds. Injury due to Zn arsenate is not reduced by adding FeS. The influence of humidity on arsenical injury to foliage is very marked even before the satn. point is reached. An increase in temp. has little effect on the action of arsenicals in a dry atm.

W. H. ROSS

**The efficacy of copper salts.** V. SEBASTIAN. *Prog. agr. vit.* **80**, 323-4(1923).—Observations on the necessity of Cu in antimildew sprays. The suggestion is made that the action of Cu may be due to soln. of the cellulosic membrane of the conidia cells in a manner similar to the action of Schweitzer's reagent. P. R. D.

**Mixture consisting of lime-sulfur or polysulfides of calcium as insecticide or fungicide.** BRUTTINI. *Report* 36 pages, Rome, 1920; *Bull. Agr. Intelligence* **11**, 525-7 (1921).—A highly concd. soln. of lime-sulfur is manufd. from S, which is recovered in the purification of illuminating gas. The product has a sp. gr. of 35 to 40° Bé. The use of lime-sulfur as an insecticide and fungicide is discussed at length.

JOSEPH S. HEPBURN

**Insecticide.** W. S. COX. U. S. 1,469,773, Oct. 9. A poison for boll weevil and other insects is formed of chloride of lime 4 and Paris green 1 part by vol.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**Diastase from the technical aspect.** W. L. MOSE. *Chem. Eng. Mining Rev.* **15**, 328-30(1923).—A discussion of the action of diastase on starch and methods of prepn. of malt. E. F. PERKINS

**Disease ferments in the vinegar industry.** G. MEZZADROLI. *L'Italia vinicola agraria* **10**, 102-4, 154-64(1920); *Bull. Agr. Intelligence* **11**, 786-7(1921).—Eel worms (*Rabditis aceti*) commonly, bacteria rarely, infect the medium during the manuf. of vinegar. In case of bacterial infection, the fermentation vats should be treated with SO<sub>2</sub>, then washed with pure water. The wine should be pasteurized, then inoculated with a tested culture of the acetic ferment.

JOSEPH S. HEPBURN

**Detection of cider in wine.** CARINO-CANINA. *Giorn. vinicolo ital.* **46**, 164-6 (1920); *Bull. Agr. Intelligence* **11**, 1187-9.—Apple must and grape must cannot be distinguished from each other by means of their content of gums and pectin since these substances are present only in small quantities. The following test is recommended. A concd. soln. of KNO<sub>3</sub> and NaNO<sub>3</sub> is added to 15 cc. of wine; if cider be present, the liquid assumes a color ranging from dark green to blackish brown, and black flakes appear in a short time; these flakes are insol. in water and alc., but dissolve in alkalies with the production of a red color. White wines made from grapes yield an orange or dark yellow color in this test, but a ppt. does not form. The test is less decisive in the case of red wines on account of their pigment. The reaction is retarded by sulfurous acid, but is not influenced by pasteurization.

JOSEPH S. HEPBURN

**Absolute alcohol by rectification with glycerol.** J. SCHNEIBLE. U. S. 1,469,447, Oct. 2. Alc. is dehydrated by passing its vapors in a rectifying column into contact with glycerol which is at a higher temp. than that of the alc. vapors.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Estimation of easily dehydrated alcohols in essential oils.** L. S. GLITCHICH. *Bull. soc. chim.* **33**, 1284-96(1923).—See C. A. **17**, 3226. E. J. C.

**John Uri Lloyd.** M. H. FISCHER. *Ind. Eng. Chem.* **15**, 1194(1923).—A brief biography, with portrait. E. J. C.

**Neutral acriflavine.** A. A. MOORE. *Dental Cosmos* **65**, 984-6(1923).—A comprehensive discussion of neutral acriflavine as an antiseptic. JOSEPH S. HEPBURN

**Dentifrices.** M. H. ITTNER. *Northwest J. Dentistry* **11**, No. 5, 3-9(1923).—The best dentifrice for general use has a mildly alk. reaction, and contains soap and non-cryst. CaCO<sub>3</sub>. Ca phosphate is too hard for such use. Glycerol, in the concn. used, imparts softness to a paste but has no harmful action on the tissues. An acid dentifrice is not advisable. The *p<sub>H</sub>* of the saliva varies with the individual, ranging from 6.0 to 7.1 with an av. value 6.5. Use of alk. and acid dentifrices yielded similar results; the acidity of the saliva was temporarily decreased, then returned to its initial value, frequently in 5 min., usually in 15 min., always in less than 30 min. Both types of dentifrice increased the flow of saliva, and neither type had any lasting effect on its ptyalin action. Continuous chewing of paraffin produces a flow and alkalinity of the saliva more marked than that evoked by any dentifrice. JOSEPH S. HEPBURN

**Italian camphor.** F. CAVARA. *Riv. ital. essenze profumi* 2, 43 (1920); *Bull. Agr. Intelligence* 11, 726-8 (1921).—The leaves of *Laurus camphora* grown in Italy are richer in camphor than those from any other country; the dried leaves contain 2.4 to 3.0% camphor. Fallen leaves may be used for the recovery of camphor. Italian leaves yield camphor and camphor oil in the ratio of 2:1. Italian branches and trunk roots contain less camphor than those from Japan.

**Van Ess special dandruff massage.** ANON. *J. Am. Med. Assoc.* 81, 1460 (1923).—Van Ess is sold by the Van Ess Laboratories, Chicago. It is guaranteed to make hair grow. A four-oz. mixt. retails for \$1.50. Analysis shows: kerosene 36, EtOH 14, quinine sulfate 0.06 and H<sub>2</sub>O, perfume and dye to make 100%.

L. E. WARREN

**Assay of digitalis by intramuscular injection in the frog.** M. S. DOOLEY AND C. D. HIGLEY. *J. Am. Pharm. Assoc.* 11, 944-7 (1922). The present official method of digitalis assay is unsatisfactory because absorption from the lymph sac is not uniform. D. and H. describe a method involving intramuscular injection in the frog which is simpler than the official method and which gives more uniform results. The dose is smaller and the end point sharper than in the lymph sac method. The rate of elimination is an important factor in the frog as in mammals. It is probable that the rate of elimination of drugs in the frog, as in mammals, plays an important role in the final result. It is believed that the great variability of many presumably assayed com. preps. is due to reliance having been placed on the method of injection into the lymph sac. The better absorption from the muscles is due to division of the dose, better blood supply, and movements of the animals.

L. E. WARREN

**Deterioration of the tincture of digitalis.** CHAS. C. HASKELL, D. S. DANIEL AND G. S. TERRY. *J. Am. Pharm. Assoc.* 11, 918-22 (1922). *Digitalis purpurea* was grown in Virginia in 1916. Tinctures were prepd. from 4 lots in 1917 and each was immediately tested by the Hatcher cat method. The tinctures were kept for 5 yrs. in tint. cork-stoppered bottles under conditions about such as would be encountered in drug stores, small portions being removed occasionally. In 1922 the tinctures were reassayed by the cat method. The findings indicated that the preps. had undergone no appreciable change. The stability of tincture of digitalis, as judged by reports in the literature on the assays with the 1-hr. frog method and the guinea pig method, is discussed.

L. E. WARREN

**Study of a digitalis substance which is eliminated rapidly after its intravenous injection in the cat.** SOMA WEISS AND R. A. HATCHER. *J. Am. Pharm. Assoc.* 12, 26-39 (1923).—The evidence that tinct. of digitalis contains a substance that is eliminated rapidly following its intravenous injection in the cat is supported by the results. This substance has been obtained from the tinct. from CHCl<sub>3</sub> exts. of the infusion, from digitoxin-Keller, so-called, and from a com. prepn. This substance can be prepd. in an impure state in a degree of activity approximating that of cryst. digitoxin, about half as active as digitoxin for cats by intravenous injection, and about  $\frac{1}{2}$  as active as digitoxin when tested on frogs. It has been shown to have a true digitalis action by causing it to induce systolic standstill of the ventricle of the frog heart, and by showing that it is qualitatively synergistic with ouabain. It gives some of the color reactions supposed to be characteristic of digitoxin. A nearly fatal dose is eliminated within a few hrs. following its intravenous injection into the cat, whereas the action of a nearly fatal dose of digitoxin persists for several weeks. Its mode of elimination is unknown. The solubilities have been studied, but since the substance is impure, the results are only of suggestive value, and probably only qual. It is especially interesting to observe that several CHCl<sub>3</sub> percolates of digitalis—but not all of them—consist almost wholly of the rapidly eliminated fraction, in contrast to digitoxin. The CHCl<sub>3</sub> sol. substance extd. from the infusion contains a variable amt. of this rapidly eliminated fraction, in contrast to digitoxin. The CHCl<sub>3</sub> sol. substance extd. from the infusion contains a variable amt. of this rapidly eliminated fraction from which it may be freed almost completely by washing it with Et<sub>2</sub>O. The amt. of the rapidly eliminated fraction present in the CHCl<sub>3</sub> sol. substance can be estd. fairly accurately by means of the differential test on the cat. This test consists in detg. the smallest fatal dose by rapid intravenous injection, and the % of activity which persists after an interval of several hrs. following the injection of a given dose. It is of clinical importance to det. the % of rapidly eliminated substance in digitalis preps., in addn. to estg. the total toxicity. W. and H. believe that many of the difficulties concerned in the investigation of digitalis require the cooperation of the clinician, the chemist, and the pharmacologist.

L. E. WARREN

**Solution of chlorinated soda.** E. F. KELLEY AND J. C. KRANTZ, JR. *J. Am.*



*Pharm. Assoc.* 12, 112-4(1923).—Mix 20 g. of NaOCl with 400 cc. of H<sub>2</sub>O. Dissolve 20 g. of anhyd. Na<sub>2</sub>HPO<sub>4</sub> in 400 cc. of H<sub>2</sub>O at 50° and pour the soln. into the NaOCl soln. Shake and allow to stand for 15 min. Transfer the ppt. to a filter and wash it with H<sub>2</sub>O until the filtrate measures 1000 cc. The prepn. contains about 0.5% of NaOCl. It does not become pink on standing and is as stable as other solns. of corresponding strength prepd. by other methods.

L. E. WARREN

**Chemically pure anhydrous dextrose should be official in the United States Pharmacopeia.** J. L. MAYER. *J. Am. Pharm. Assoc.* 12, 115-6(1923).—Presentation of arguments.

L. E. WARREN

**The diffusion of phenol and tricresol through rubber.** PETER MASUCCI AND MARGARET I. MOFFAT. *J. Am. Pharm. Assoc.* 12, 117-20(1923).—Aging expts. covering 18 mo. show that rubber-capped biological products contg. 0.3% tricresol or 0.5% C<sub>6</sub>H<sub>5</sub>OH lose a part of their preservative by diffusion through the rubber. The loss is 50-70% for tricresol and 20-40% for C<sub>6</sub>H<sub>5</sub>OH. In certain cases the rubber caps coming in contact with C<sub>6</sub>H<sub>5</sub>OH gave a blue color on standing. The color appears to be due to some reaction between the C<sub>6</sub>H<sub>5</sub>OH and C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> present as a result of vulcanization.

L. E. WARREN

**Further notes on tincture of cantharides.** F. W. NITARDY. *J. Am. Pharm. Assoc.* 12, 140-2(1923); cf. *C. A.* 14, 1003; 16, 2963. —Cantharides was extd. with EtOH, CHCl<sub>3</sub>, glacial C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> and acetone or mixts. of 2 or more of these solvents and the finished products were tested by trials on the human arm. The results indicated that tinctures obtained by extn. with mixts. of EtOH and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> are satisfactory. The minimum % of C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> necessary to produce the most satisfactory tincture was not detd.

L. E. WARREN

**Aqueous and alcoholic elixirs versus aromatic elixirs.** CLYDE M. SNOW AND BERNARD FANTUS. *J. Am. Pharm. Assoc.* 12, 143-6(1923).

L. E. WARREN

**Cymene from oil of *Monarda punctata*.** J. M. JOHNSON, H. MERRITT AND R. E. KREMERS. *J. Am. Pharm. Assoc.* 12, 222-5(1923).—Oil of *Monarda punctata* contains about 50% of substances other than menthol. Cymene is found in the non-phenol portions. Fractionation of this portion did not yield pure cymene. The portion, b. 170-5° was shaken with 1% KMnO<sub>4</sub> and steam distd. The recovered oil was dried over Na<sub>2</sub>SO<sub>4</sub> and distd. Three fractions were obtained, b. 173-7°, d<sub>4</sub> 0.853, n<sub>D</sub><sup>20</sup> 1.4838-61. *N*-Phenylcymenesulfonamide, m. 127-8°. *N*-Naphthylcymenesulfonamide, m. 103-4°. *N*-Cymyl-2-cymenesulfonamide, m. 117-8°.

L. E. WARREN

**2-Nitro- and 2-aminocymene.** W. A. DEMONBREUN AND R. E. KREMERS. *J. Am. Pharm. Assoc.* 12, 296-300(1923); cf. preceding abstr. —Much difficulty was found in nitrating the cymene. The method adopted is: 67 g. of H<sub>2</sub>SO<sub>4</sub> are placed in a heavy porcelain beaker packed in ice, 67 g. of cymene added and the mixt. is stirred until 0° is reached. A cooled mixt. of 105 g. of H<sub>2</sub>SO<sub>4</sub> and 50 g. of HNO<sub>3</sub> is added drop by drop with const. stirring. NaCl is added to the ice occasionally. About 6 hrs. are required for the reaction. The mixt. is stirred 30 min. longer and poured into an equal vol. of cold H<sub>2</sub>O. The oily layer is washed twice with H<sub>2</sub>O and fractionated. The heavier fraction was dried over CaCl<sub>2</sub> and distd. *in vacuo*; b<sub>14</sub> 130-5°; d<sub>20</sub> 1.0355; n<sub>D</sub><sup>20</sup> 1.5290. 2-Aminocymene was prepd. by Sn and HCl in the usual way, and by Fe and HCl; d<sub>4</sub> 0.9448; n<sub>D</sub><sup>20</sup> 1.5395. The HCl deriv. m. 206-7° and the acetyl compd. at 70-1°. L. E. W.

**The biological standardization of local anesthetics, with special reference to the effect of sterilization on solutions of cocaine and procaine.** P. S. PITTINGER. *J. Am. Pharm. Assoc.* 12, 229-33(1923).—Continuation (cf. *C. A.* 16, 4014). P.'s method was applied to check the effect of aging and the various forms of sterilization upon solns. of cocaine and procaine. Solns. of a cocaine salt and procaine were prepd. such that each cc. contained the minimum quantity of anesthetic which would produce local anesthesia in 5 min. The concn. for cocaine was 0.6% and for procaine 7.07%. Portions of these solns. were kept in ampoules under a variety of conditions, sterilized, unsterilized, or preserved by the addn. of antiseptics. Portions were tested immediately after filling and at 3 mo. intervals. Portions of the original dry salts were also kept and fresh solns. prepd. from them and tested at intervals. The activity of solns. of cocaine and procaine is not affected by the addn. of 0.3% soln. of a mixt. of the 3 cresols or by sterilization by means of the Arnold sterilizer or autoclave at 115° for 15 min. Unsterilized solns. of cocaine and procaine, solns. sterilized without heat and solns. sterilized with heat apparently lose no activity during a period of 3 mos. Unsterilized solns. of cocaine and solns. sterilized without heat apparently lose about 10% of their activity during a period of 14 mos. Solns. of cocaine which have been autoclaved for 15 min. at 115° apparently lose no activity

during a period of 14 mos. Solns. of cocaine which have been Arnold-sterilized apparently lose about 5% of their activity during a period of 14 mos. Unsterilized solns. of procaine, solns. sterilized without heat and solns. sterilized with heat lose no activity during a period of 14 mos. Cocaine and procaine in the dry form are apparently stable and show no signs of deterioration during 14 mos. Concd. solns. of cocaine or procaine can be sterilized 5 successive times at 115° without any apparent loss of activity.

L. E. WARREN

**A method for assaying unguentum stramonii.** A. R. BLISS, JR. AND M. F. BROWN. *J. Am. Pharm. Assoc.* 12, 240-1 (1923).—Introduce 30 g. of ointment of stramonium into a 250-cc. centrifuge flask. Then add 150 cc. of a mixt. of Et<sub>2</sub>O, 2 vols., and CHCl<sub>3</sub>, 1 vol., followed by 10 cc. of ammonia water. Shake the mixt. vigorously until all fatty matter is dissolved, and then continue the shaking for 3 hrs. on a mech. shaker. Allow the mixt. to stand until complete sepn. has taken place, and then decant 100 cc. of the clear liquid, representing 20 g. of the ointment, into a separator. Ext. the alkaloids from the soln. in the separator by shaking out repeatedly with weak H<sub>2</sub>SO<sub>4</sub> until the alkaloids are completely removed. Collect the acid washings in a separator, add NH<sub>4</sub>OH until the soln. is decidedly alk. to litmus, and completely ext. the alkaloids by shaking out repeatedly with CHCl<sub>3</sub>. Evap. the combined CHCl<sub>3</sub> washings to dryness, dissolve the residue in exactly 5 cc. of 0.1 N H<sub>2</sub>SO<sub>4</sub> and titrate the excess of acid with 0.02 N KOH, using cochineal as indicator. The method gives accurate results.

L. E. WARREN

**Hot extraction of drugs.** W. L. SCOVILLE. *J. Am. Pharm. Assoc.* 12, 241-5 (1923).—Hot extn. was tried on 6 drugs. Those which contained H<sub>2</sub>O in the menstruum were extd. in a percolator provided with a jacket and reflux. Drugs contg. a considerable proportion of albuminous matter which is coagulated by heat, and which are extd. with an aq. or weakly alcoholic menstruum are better extd. by the hot menstruum. Licorice, vanilla and nux vomica are examples—the latter 2 when extd. with weakly alcoholic menstrua or with H<sub>2</sub>O. Drugs contg. a material proportion of starch are not helped by hot extn. because the heat gelatinizes the starch and makes the drug impermeable. This was proved especially on ipecac. Cinchona, a drug which contains much tannoid matter and which needs HCl for the rapid extn. of its alkaloids, has its tannoid substances changed to phlobaphenes by the action of the dil. HCl, and the drug then clogs and refuses to allow the menstruum to pass through it. Heat hinders rather than favors extn. in this case. Physostigma, which needs a highly alcoholic menstruum, is helped some by hot extn. But quite as good results are obtained in this case by cold percolation through a finer powder, and by the use of more acid menstrua. For strongly alcoholic menstrua finer powders are needed in all cases than for aq. menstrua and the heat is likely to induce loss of menstruum, which will offset economy in percolate. In general hot extn. is better applied when aq. menstrua are used and coarser powders employed. It is likely to be inapplicable to starchy drugs because of the gelatinizing of the starch and the hindrance to penetration of the drug by the hot menstruum by this action. Drugs contg. albuminous matters give clearer and more stable preps. by hot extn.

L. E. WARREN

**Fluidextract of ergot.** J. P. SNYDER. *J. Am. Pharm. Assoc.* 12, 246-8 (1923).—Fluidextract of ergot was prepd. by several methods, assayed, stored for some time and reassayed. Defatting the drug by CCl<sub>4</sub> before percolation gives a product which gives but little ppt. on standing. This solvent is much better than melted paraffin. Defatting the drug does not cause loss of therapeutic activity in the fluidext. or hasten its deterioration.

L. E. WARREN

**Occurrence and forms of calcium oxalate crystals in official crude drugs.** E. T. WHEBBY AND G. L. KEENAN. *J. Am. Pharm. Assoc.* 12, 301-18 (1923).—About 75 official drugs contain crystals of CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O. The object of the study was to det. whether the crystals actually possessed the properties of ordinary CaC<sub>2</sub>O<sub>4</sub>. A specimen of each crude drug was reduced to powder, and a minute quantity was placed on a microscope slide. This was moistened with a tiny drop of an oily liquid having the refractive index of 1.650, attention being given to the distribution of the material in the liquid, and the cover glass was applied. The slide was examd. under a microscope provided with a revolving stage, nicol prisms, cross-hairs in the eyepiece parallel to the vibration planes of these nicols, and a substage diaphragm. Crystals were located in the mass by search with the nicols crossed, so that most of the field was dark. Exams. were made by the immersion method under the petrographic microscope. Various liquids were used as immersion fluids to produce indexes of refraction of any value desired. The liquid most used consisted chiefly of C<sub>10</sub>H<sub>7</sub>Br contg. a little C<sub>10</sub>H<sub>7</sub>Cl. Tetragonal CaC<sub>2</sub>O<sub>4</sub> was found in hyoscyamus. It is found in several other plants. It is probably

a trihydrate.  $\text{MgC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  has been found in the pericarp of black pepper, but it was not found in any of the official drugs.  $\text{KHC}_2\text{O}_4$  has been found in some plants but it has not been reported in any of the official drugs. The findings for 116 drugs which contain  $\text{CaC}_2\text{O}_4$  are recorded. The observations for each drug cannot be abstracted.

L. E. WARREN

#### Reduction of Bi by dextrose (COUSIN) 7.

**Absorbing radium emanations.** H. B. PALMER. U. S. 1,470,027, Oct. 9. A gas such as air is passed through a soln. of caustic alkali to free it from  $\text{CO}_2$ , then through a column of radioactive soln., and then through a column of  $\text{H}_2\text{O}$  to absorb the emanation from the gas. The soln. thus obtained may be used for therapeutic purposes.

**Apparatus for preparing anesthetics.** L. STEINER. U. S. 1,469,608, Oct. 2. Freezing of ether or similar anesthetics during volatilization is prevented by admixt. of heated air.

### 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

**Tests on gas from pyrites burners.** ERICH RICHTER. *Wochbl. Papierfabr.* 54, 1521-24(1923).—The reaction between concd. KI soln. and  $\text{SO}_2$  is inaccurate for the testing of pyrite burner gas. The ordinary absorption app. gives continually deviating values for  $\text{SO}_2$ . An app. is described in which the gas to be tested is slowly passed through a cold condensation tube, whereby the  $\text{SO}_2$  is condensed and subsequently detd. in the usual gravimetric way. Comparative results for  $\text{SO}_2$  were obtained.

J. L. PARSONS

**Synthesis of ammonia by the Fauser process.** A. ZAMBIANCHI. *Can. Chem. Met.* 7, 253-4(1923). See C. A. 17, 3405.

E. J. C.

**Experiments on the arc process for nitrogen fixation.** E. D. MCCOLLUM AND FARRINGTON DANIELS. *Ind. Eng. Chem.* 15, 1173-5(1923).—With const. power input to the arc high voltage gave the highest yield. Interrupting the arc or increasing the velocity of the air stream did not increase the yield and modifying the arc with a condenser decreased it. *Silica gel* proved an admirable adsorbent for N oxides, and on heating gave them up quant.

F. C. Z.

**Our nitrogen problem.** H. A. CURTIS. *Chem. Age (N. Y.)* 31, 388-91(1923).—A popularized review. The export tax on nitrate from Chile is \$11.25 per short ton, 25 to 40% of the total cost on board ship.

F. C. Z.

**Texas potash.** MEIGS, BASSETT AND SLAUGHTER. *Chem. Age (N. Y.)* 31, 395-8(1923).—An abstr. of a report compiled for the Bur. of Economic Geology and Technology, Division of Economic Geology, Univ. of Texas. Detailed figures are given for a plant to make  $\text{KCl}$ ,  $\text{NaCl}$  and  $\text{MgO}$  or  $\text{MgCO}_3$  from the brine obtained from wells in the Llano Estacado.

F. C. Z.

#### $(\text{NH}_4)_2\text{SO}_4$ (Brit. pat. 197,315) 10.

**Phosphoric acid.** S. PEACOCK. U. S. 1,468,741, Sept. 25.  $\text{Ca}_3(\text{PO}_4)_2$  is reacted upon with 6 mol. proportions of  $\text{NaCl}$  at a temp. of about  $1100^\circ$  in order to form  $\text{POCl}_3$  and  $\text{Na}_2\text{O}$ . The chloride formed is sepd. from the oxide and is treated with  $\text{H}_2\text{O}$  to form a mixt. of  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$  and the latter is separately recovered.

**Separating potassium and calcium chlorides.** W. GLABER. U. S. 1,469,507, Oct. 2. A mixt. of chlorides of K and Ca such as is obtained by heating K-bearing silicates with  $\text{CaCl}_2$ , C and  $\text{Fe}_2\text{O}_3$  is heated with steam and  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{KCl}$  is leached out of the residue.

**Apparatus for the continuous manufacture of aluminium chloride.** F. W. HALL. U. S. 1,468,632, Sept. 25. A vertical retort is heated by a surrounding combustion chamber and a discharge for spent material leads from the retort into the combustion chamber at the bottom of the retort. Ash from the retort serves to maintain a gas-tight seal about this outlet.

**Evaporating apparatus adapted for treating brines.** E. WIRTH-FREY. U. S. 1,469,475, Oct. 2.

**Recovering sulfur dioxide from blow-pit vapors and gases.** C. A. RICHTER. U. S. 1,469,958, Oct. 9. Blow-pit vapors and gases are conducted in countercurrent contact

with cold  $H_2O$  through a mass of inert rock or similar contact material to cool the gases and condense vapors. Free unabsorbed  $SO_2$  which has been cooled by the  $H_2O$  is recovered and the  $SO_2$  absorbed by the heated  $H_2O$  is then removed from it.

**Sulfur dioxide from burner gases.** G. A. RICHTER and G. F. WIGHTMAN. U. S. 1,469,959, Oct. 9. Hot S burner gases and cold  $H_2O$  are brought into contact by counter-current flow and the cooled gases are passed through an absorbing medium such as  $CaCO_3$  and  $MgCO_3$  to recover  $SO_2$ . A gas such as part of the spent gas from the absorption is passed through the  $H_2O$  used for cooling the hot burner gases to remove  $SO_2$  from the  $H_2O$  and the recovered  $SO_2$  is mixed with the cooled gases.

**Open pans for burning sulfur.** W. H. KOBBE. U. S. 1,469,644, Oct. 2.

**Sulfur burner.** W. H. KOBBE. U. S. 1,469,645, Oct. 2. Pans for burning S are provided with slots in their sides to receive corners of overlying pans when the pans are stacked in a burner.

**Abrasive coatings.** F. J. CREPT. U. S. 1,468,960, Sept. 25. A backing such as paper or cloth is coated with a glue soln. and abrasive material is attached to the glue coating. An overlying coating of a compn. formed from rosin 250, glue 60, PhOH 65, HOAc 56, benzene or  $C_6H_6$  5 and  $H_2O$  166 parts is then applied in order to waterproof the surface.  $CH_2O$  is also preferably used.

**Coating for airplane wings.** K. KAWASHIMA. U. S. 1,469,839, Oct. 9. Nitrocellulose is treated with an aq. soln. of  $H_3PO_4$  and  $H_2O_2$  to effect partial denitration and is then dissolved in acetone.  $H_3BO_3$  and  $MgCl_2$  are added to the soln. to render the coating formed more resistant to temps. up to 200°.

**Finishing walls or art goods.** E. MUEHLBAECKER. U. S. 1,470,182, Oct. 9. Walls or articles of Fe, stone or wood are coated with a mixt. of  $CaCO_3$  and shellac and then subjected to the flame of a blow torch to produce a roughened artificially aged or antique finish.

**"Electrical cement."** A. P. SULLIVAN. U. S. 1,468,930, Sept. 25. A cement adapted for attaching pig-tails to elec. brushes is formed of Cu powder together with less than one-fourth its amt. of  $MgCl_2$  and  $MgO$ .

**Apparatus for hydrating lime.** D. R. BONE. U. S. 1,469,201, Oct. 2. Lime from a kiln outlet is carried by cars to a body of  $H_2O$  into which the cars and contents are immersed.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**The manufacture of optical glass.** C. J. PEDDLE. *Trans. Optical Soc. (London)* 23, 103-30(1922) (13 figs. and 12 reproductions of photographs).—This paper describes briefly the history of optical glass manuf. from the earliest attempts to date. The present methods of manuf. in Great Britain are then described in more detail. Only 50% of the glass usually passes the preliminary inspection and if 20% of the total is usable after finishing, the melt is considered satisfactory. The yield is often under 10%. "The only sure method of testing for fine striae in glass is the examn. of pieces of glass, polished on opposite faces, by means of a polariscope." P. has studied the influence of compn. upon d., n, durability and tendency to devitrification (cf. C. A. 14, 2536, 2569; 15, 2066; 16, 620, 3180), and these are discussed. The effect of different oxides on the d. of glass depends on the mol. wt. of the oxides. In glasses of compn.  $100SiO_2, 20 Na_2O, 10RO$  the ds. and mol. wts. are in the following order  $RO \rightarrow PbO$  (223),  $BaO$  (153),  $SrO$  (104),  $ZnO$  (81),  $CaO$  (56),  $MgO$  (40); ds. of glasses are 2.91, 2.71, 2.57, 2.52, 2.46 and 2.39, resp. The curves illustrate the connection between the phys. properties and chem. compn. of glasses. Durability of the glasses was tested by the action of water at 80° on the powd. glass.  $ZnO$  effects the greatest improvement of durability when replacing  $SiO_2$  or  $R_2O$  wt. for wt. The  $RO$  oxides improve durability in order of their mol. wt.,  $MgO$  being best and  $PbO$  worst. Photographs are given of crystals formed in the devitrification of glasses. The paper includes a short bibliography.

DONALD E. SHARP

**Hydrogen-ion concentration of different kinds of glassware when sterilized with buffered and non-buffered solutions.** F. W. FABIAN and R. C. STULL. *Abstracts Bact.* 5, 210(1921).—Glassware from stock, filled with a non-buffered soln. (cond. water) and autoclaved for 30 min. at 15 lbs. pressure, yielded sufficient alkali to change the  $pH$  of the soln. from 7.0 to 9.8. When the expt. was repeated, with a buffered soln. (nutrient broth), the  $pH$  was not appreciably changed. Upon autoclaving, soft glass

yielded more alkali than hard glass. Glass, which has been treated with  $\text{CrO}_2\text{-H}_2\text{SO}_4$ , cleaning soln., still gives up alkali on autoclaving. JOSEPH S. HEPBURN

Electrification of the Allegheny Plate Glass Co. G. P. WILSON. *Glass Ind.* 4, 127-9, 152-3, 169-72(1923); 8 illus. J. B. PATCH

Furnace and combustion calculations. H. S. BRADY. *Glass Ind.* 4, 148-52 (1923).—The method is given for figuring the saving effected by cutting down the excess of air in a gas furnace. J. B. PATCH

Initial heat leers. W. S. MAYERS. *Glass Ind.* 4, 163-6(1923); 3 figs.—This leer is somewhat analogous to the fireless cooker. The ware is introduced immediately as it issues from the mold while still red hot and with a min. amt. of cooling. Two gas burners (or oil) heat the pans and prevent bottom checking. The initial heat of the ware is preserved by suitable insulation and the annealing time is reduced to  $\frac{1}{4}$  of that of the existing type of leers, thus allowing the leer size to be cut proportionally and the fuel consumption to a small fraction. J. B. PATCH

New glass furnace types in England and Europe. H. W. HESS. *Glass Worker* 42, No. 44, 11, 38-40(1923). J. B. PATCH

Polishing glass with acid. O. PARKERT. *Diamant* 45, 165, 177(1923); cf. C. A. 16, 1139.—The ware is first washed in a bath of  $\text{H}_2\text{O}$  1000,  $\text{H}_2\text{SO}_4$  12, and  $\text{HCl}$  1. It is then dipped for about 45 sec. in a soln. of  $\text{H}_2\text{O}$  1,  $\text{H}_2\text{SO}_4$  2, and  $\text{HF}$  1, preferably kept at a temp. of 40-50°. J. B. PATCH

The manufacture of glass marbles. C. J. STAHL. *Glashütte* 53, 356-7, 371-2, 403-4, 419-21, 435-6(1923). J. B. PATCH

The mechanical strength of glazing glass. A. E. WILLIAMS. *J. Am. Ceram. Soc.* 6, 980-8(1923).—About 5000 samples of various types of glass were tested. The modulus of rupture of various kinds averaged: window glass, single and double strength and 26 oz. clear sheet glass, 7000; clear sheet glass, 29 to 39 oz. and  $\frac{1}{4}$  inch. plate glass, 6500; rolled sheet and wire glass, 6500; ribbed rolled sheet and wire glass, 5300; corrugated wire glass, 1 in. deep, 13,500; same  $\frac{3}{4}$  in. deep, 9500 lbs. sq. in. Young's modulus averaged: single and double strength window glass, 11,000,000; 26 to 39 oz. clear sheet glass, 10,500,000; polished plate glass, 10,000,000; rough rolled glass, 970,000; non-scatterable glass (varies greatly with thickness)  $\frac{1}{16}$  in., 18,670,000; same  $\frac{1}{4}$  in., 550,000 lbs. sq. in. C. H. KERR

Glass decorators palette and its preparation. T. LENCHNER. *J. Am. Ceram. Soc.* 6, 1040-3(1923). C. H. KERR

Substituting fuel oil for producer gas in a continuous glass tank. F. S. THOMPSON. *J. Am. Ceram. Soc.* 6, 1050-5(1923). C. H. KERR

Effect of hydrogen-ion concentration upon clay suspensions. F. P. HALL. *J. Am. Ceram. Soc.* 6, 989-99(1923).—Generalizations are difficult. All ball clays do not give a more acid water ext. than all kaolins, or *vice versa*. A greater knowledge of the isoelec. point and the point of max. deflocculation would be of great value in purification processes, casting, etc. The action of alkali on clay over the range  $p_H$  7-12 can be explained in certain cases as due primarily to adsorption. Above  $p_H$  12 the action seems to be chem. rather than phys. ( $p_H = \log 1/\text{H}^+$ ;  $p_H$  of pure  $\text{H}_2\text{O} = 7.0$ ). A soln. with  $p_H$  less than 7 is acid while one with  $p_H$  greater than 7 is alk. Methods used for measuring  $\text{H}^+$  and  $\text{OH}^-$  concns. of aq. solns. are given and data are tabulated. C. H. KERR

The quantity and composition of colloid clay in kaolin from Meissen. ALBERT VASEL. *Kolloid-Z.* 33, 178-80(1923).—The Meissner kaolin contained at least 3% of colloid clay whose compn. corresponded to the theoretical formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Lime and magnesia did not enter into the compn. of the clay substance but were adsorbed by the colloid particles. H. M. McLAUGHLIN

Construction features of importance in clay plants. T. W. GARVE. *J. Am. Ceram. Soc.* 6, 961-71(1923). C. H. KERR

Tests on some sagger clays and bodies. R. TWELLS, JR. *J. Am. Ceram. Soc.* 6, 949-57(1923).—Three typical clays and 2 series of bodies were tested. The best body of the fire clay-grog type was: No. 8 buff clay 29.8, No. 1 fire clay 18.2, grog (6-20 mesh) 42.0, grog (20 mesh and finer 10.0%). Of 100 saggars made from this body only 3 were broken and 15 slightly cracked after 5 burns. A superior special body was: Georgia kaolin 35, Tenn. ball No. 5 10, Grog (10-40 mesh) 55%. Another superior special body was: Kentucky ball clay No. 4 40, medium sized  $\text{SiC}$  firesand 60%. Plant trials showing cost per fire may show the special bodies to be the cheapest in the end. C. H. KERR

Automatic kiln stokers. J. D. MARTIN. *J. Am. Ceram. Soc.* 6, 1044-9(1923). C. H. KERR

**Fuel oil as adapted to the chambered continuous kiln.** M. A. TAYLOR. *J. Am. Ceram. Soc.* 6, 1056-61(1923). C. H. KERR

**Experiences with Dutch kilns.** R. A. HORNING. *J. Am. Ceram. Soc.* 6, 958-60(1923).—Setting and burning are described. C. H. KERR

**Insulation of periodic kilns.** J. H. KRUSON. *J. Am. Ceram. Soc.* 6, 1069-71(1923).—Great savings are made by proper insulation. C. H. KERR

**Progress report on specifications for refractories.** R. F. GELLER. *J. Am. Ceram. Soc.* 6, 1098-1111(1923).—Tests were made on 41 brands of com. bricks. Service tests also are under way. A mass of data is tabulated and shown by graphs. The endurance test (72 hrs. at 1450°) is hard to make and not of great value. The const. vol. test (5 hrs. at 1400°) gives valuable adsorption data. The quenching test from 850° is an excellent test. Dctn. of fusion point is of first importance. The load test is of value in special cases but apparently need not always be made. Chem. analysis furnishes valuable information. C. H. KERR

**The transfer of heat through refractories and its determination.** A. S. WATTS AND R. M. KING. *J. Am. Ceram. Soc.* 6, 1075-89(1923).—A lab. testing equipment is described. Comparative heat transfer values were detd. as: alundum No. 1, 1.000; alundum No. 2, 0.977; sil-o-cel, 0.263; carbofrax B (92% SiC), 3.39; magnesite 2.33. C. H. KERR

**The requirements of fire brick suited to malleable practice.** H. A. SCHWARTZ AND A. F. GORTON. *J. Am. Ceram. Soc.* 6, 1094-7(1923). C. H. KERR

**Metallurgical requirements of refractories for use in the aluminum industry.** ROBERT J. ANDERSON. *J. Am. Ceram. Soc.* 6, 1090-3(1923). C. H. KERR

**An electric furnace for vitreous enameling.** C. SCHWIER. *J. Am. Ceram. Soc.* 6, 1030-9(1923).—A Westinghouse furnace, is described. It is built with round wire coils placed in top, bottom and both sides. Cost data are given. C. H. KERR

**Method of cooling enamel by compressed air.** A. MALINOVSKY. *J. Am. Ceram. Soc.* 6, 972-3(1923).—It is cheaper and better than water-quenching. C. H. KERR

**Air-cooled versus water-quenched enamels.** S. WIESTER. *J. Am. Ceram. Soc.* 6, 973-5(1923).—At the Malleable Iron Range Co., Beaver Dam, Wis., the change from water to air cooling gave an enamel more resistant to smoke and flue gases and to shocks in mounting and in use. C. H. KERR

**The relations between composition and properties of enamels for sheet steel.** R. R. DANIELSON AND B. T. SWEELY. *J. Am. Ceram. Soc.* 6, 1011-29(1923).—Replacing  $B_2O_3$  by  $Na_2O$  increased the coeff. of expansion and decreased fish-sealing. The compressive strength of the ground coats decreased when  $B_2O_3$  was replaced by  $Na_2O$  but the reverse was true with cover enamels. Impact on solid parts gives an index of the toughness but impact on corners, etc., shows inherent strength of the enamel rather than its "fit" on the ware. For max. resistance to thermal shock the coeff. of expansion of the ground coat should equal or preferably exceed that of the cover enamel. Acid resistance, while dependent upon compn., is not affected in the same way for all enamels—in those studied the resistance decreased when  $B_2O_3$  was replaced by  $Na_2O$ . C. H. KERR

**Sandblast castings to be enameled.** J. G. JAEGER. *J. Am. Ceram. Soc.* 6, 976-9(1923).—Sandblasting methods are described. C. H. KERR

**The chemistry of the terpene medium for ceramic liquid gold.** P. P. BUDNIKOFF AND E. A. SHILOV. *J. Am. Ceram. Soc.* 6, 1000-6(1923). C. H. KERR

**Sheet glass production.** J. P. CROWLEY. U. S. 1,469,383, Oct. 2. Molten glass is supplied to a graphite-clay hopper through a slot in the bottom of which the glass flows in sheet form onto a concave graphite-clay slab which deflects the sheet onto a horizontal drawing and flattening mechanism.

**Forming sheet glass.** J. P. CROWLEY. U. S. 1,469,382, Oct. 2. A mass of glass is withdrawn from a molten body and while highly heated and plastic is bent and laterally extended by rollers and an endless apron to form a sheet.

**Machine for drawing sheet glass.** R. P. CALLARD. U. S. 1,469,379, Oct. 2.

**Machine for continuous drawing of sheet glass.** R. P. CALLARD. U. S. 1,469,380, Oct. 2.

**Condensing lenses.** M. E. TROMBA. U. S. 1,470,512, Oct. 9. Lenses for projection app. are formed of glass which is colored with U or other coloring material which will cut off ultra-violet rays without massing of color from the lens at any point in the projected light.

**Furnace for decorating ceramic ware.** J. A. JEFFERY. U. S. 1,468,947, Sept. 25.

Ceramic articles such as spark plug porcelains are heated within a porcelain-lined metal retort tube.

**Tunnel kilns for drying brick or other clay articles.** J. C. BOSS. U. S. 1,468,990, Sept. 25.

**Pottery-forming machine.** M. BURGER. U. S. 1,469,378, Oct. 2.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Effect of organic decomposition products from high vegetable content soils upon concrete drain tile.** G. R. B. ELLIOTT. *J. Agr. Research* **24**, 471-500(1923).—Concrete tile as at present made breaks down in all peat soils or when exposed to the action of peat waters. The more porous the tile the more rapidly it disintegrates, and an acid soil aids in the disintegration. A high percentage of lime in the soil delays but does not stop the decompn. of the tile. Methods are described for increasing the permanency of concrete tile in peat soils.

W. H. ROSS

**Panel tests of lime plaster.** W. E. EMLEY AND E. B. BERGER. *J. Am. Ceram. Soc.* **6**, 1007-10(1923).—Specifications covering the soundness of hydrated lime or lime putty should include: (1) examine microscopically to insure the absence of  $\text{CaO}$  ( $n = 1.81$ ); (2) wash a sample through 50 mesh. If the residue exceeds 5% it should be analyzed and if found to be anything other than  $\text{CaCO}_3$  the material should be rejected. Specifications covering the sand should show limits for  $\text{FeS}_2$ ,  $\text{NaCl}$  and org. matter.

C. H. KERR

**Composition flooring.** R. R. BUTLER. *Chemistry & Industry* **42**, 980-2(1923).—A brief, general description of use of portland and magnesite cements, bitumen, rubber, and plaster of Paris for floors. Descriptions of several patented compns. for floors are included.

RAYMOND WILSON

**Coatings that prevent end checks.** *Technical Notes* **186**, Forest Products Laboratory, U. S. Forest Service(1923).—Wood dries more rapidly from the end grain than from the side grain. The checking and splitting which is likely to occur can be prevented by the application of end coatings to retard the moisture evapn. The following coatings are recommended in the order of cheapness: to be applied cold, hardened gloss oil and air-slacked lime, Chinawood oil and barytes, linseed oil with either white or red lead, spar varnish and barytes; to be applied hot, 213-254°, coal tar pitches, rosin and lampblack, asphalts and paraffin.

ALFRED L. KAMMERER

**Practical results from the use of fluorides in the preservation of wood.** ROBT. NOWOTNY. *Z. angew. Chem.* **36**, 439-40(1923); cf. *C. A.* **8**, 1003; **15**, 1609.—A further report of the life obtained from Austrian telegraph poles treated with fluorides. After twelve years, 14,500 poles treated with  $\text{ZnF}_2$  show a failure of 24.2%. The av. life of the  $\text{ZnF}_2$ -treated poles is estd. to be 20.2% years, by the method of Malenkovic (cf. *Elektrotech. Z.* **1922**, 501). 13,000  $\text{NaF}$  poles show a removal of 11.3% after 10 years, giving an estd. av. life of 22 years. If the above estimates prove correct  $\text{NaF}$  may be considered a more effective preservative than  $\text{ZnCl}_2$ ,  $\text{CuSO}_4$ , or  $\text{HgCl}_2$ . The use of  $\text{NaF}$  alone has not become very extensive in Europe. Numerous combinations of  $\text{NaF}$  and toxic organic compds. such as dinitrophenols and cresols have been used since 1910, under the following trade names, Basilet, Triolith, Fluoxith, Fluoran and Malenit. An outline of the experience in America with  $\text{NaF}$  as a preservative is given together with a bibliography.

ALFRED L. KAMMERER

**Santa Fe treatment and care of ties.** S. D. COOPER. *Wood Preserving News* **1**, 168-71(1923).—An outline is given of tie treating practice on the Santa Fe Railway from 1885 to date. From 1885 to 1901 the Wellhouse process was employed, from 1902 to 1905 the Burnettizing process and from 1906 to 1923 creosoting by the Rueping process. The present practice is the Rueping process with a mixt. of 70% creosote and 30% petroleum for the wetter regions and a mixt. of 50% creosote oil and 50% petroleum for the arid southwestern territory. An av. of 7.5 lb. of the mixture per cu. ft. is left in the ties. It is claimed that the addition of petroleum oil of asphaltic base adds considerably to the mechanical life of the ties. All ties are air-seasoned before treatment also adzed and bored for tie plates. From experience to date it is estimated that Texas pine ties treated by the Rueping process with creosote oil (5 lb. per cu. ft.) will give an av. life of 20 years. Since 1908 the annual tie renewals per mile have been reduced from 336 to about 150.

ALFRED L. KAMMERER

Petroleum asphalts in the roofing and waterproofing industries (FINLEY) **22**. Many applications of sodium silicate suggested by its uses in the paper mill (VALE) **23**.

**Gypsum plaster.** J. W. EMERSON. U. S. 1,470,260, Oct. 9. S is used as a filling for the pores of gypsum plaster to render it hard and water-repellent when set.

**Waterproof roofing material.** C. E. RAHR and I. KIRSCHBAUM. U. S. 1,469,606, Oct. 2. A colored waterproofing material such as a mixt. of wax tailings, clay and  $H_2O$  is applied as a matrix to fill the voids in the granular surfacing of roofing and a smooth surface is formed by smoothing down the matrix and abrading the protruding upper portions of the granular material.

**Treating thin layers of wood to prevent warping.** V. H. FORSSMAN. U. S. 1,469,362, Oct. 2. A thin layer of wood is treated with a washing liquid to remove "hygroscopic and ferment substances" from a large proportion of the cells and the wood is then treated with chrome alum and  $CH_3O$  to neutralize remaining "hygroscopic and ferment substances."

**Creosote mixture for impregnating wood.** L. F. VERMEIRE. U. S. 1,469,466, Oct. 2. Creosote 70, com. 32% phenol 6, coal tar 9.5, light tar oil S and  $C_{12}H_{16}$  6.5 parts.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**The chemical structure of coal.** WALTHER SCHRAUTH. *Brennstoff-Chem.* 4, 161-4 (1923); *J. Chem. Soc.* 124, II, 502-3. —Despite the work of many investigators it is not clearly understood whether cellulose or lignin plays the chief part in the formation of coal. Likewise it is not entirely clear in what manner aliphatic assimilation products of plants can be changed into aromatic or what is more probable into unsatd. hydroaromatic substances. The fundamental unit of lignin is a keto deriv. of perhydro-9,10-benzophenanthrene in which the 3 outside benzene rings are linked up with O. This mol. possesses great activity and could through rearrangement of the  $3CO$  and  $3CH_2$  groups in the enol form give rise to the formation of esters and ethers whose presence in lignin is established. On the other hand by oxidation or hydration the formation of carboxylic acids of high mol. wt. is possible, which are similar in character to humic acids. Reduction would lead to the replacement of O in the furan ring by H. It would also be possible for other condensations to take place by which in the formation of coal new mols. of unlimited size contg. S and N would be formed; this would finally, by splitting off of  $H_2O$  and  $CO_2$  lead to products not unlike coal. By the hydrogenation of coal the presence of unsatd. groups is shown. Decompn. products formed at 400° under a pressure of 200 atm. changed the coal into a viscous tar like oil whose analysis corresponds to that of above mol. The occurrence of purely aromatic hydrocarbons such as naphthalene and anthracene as primary products of the low-temp. carbonization of coal is not to be expected, but rather alkylated phenols, hydrogenated hydrocarbons and aliphatic ketones. The higher fractions of the primary tar have not yet been given an exact examn. but the results appear to be in agreement with the above formulation, which may at least be taken as a working hypothesis.

C. T. WHITE

**Comparative engine tests with crude, acid-refined and silica-gel-refined motor-benzene.** A. C. FIELDNER and G. W. JONES. *Bur. Mines, Repts. of Investigation No. 2517*, 3 pp. (1923).—Data are given with discussions regarding the annual production of motor-benzene, its compn. and the constituents present in the crude benzene which render it unsatisfactory as an engine fuel. The acid alkali method of refining benzene is reviewed and the com. specifications usual for motor benzene are enumerated. The silica-gel method for refining benzene is outlined: The distillate up to 143° from crude benzene is agitated with 1% NaOH dissolved in an equal wt. of  $H_2O$ . After settling for  $\frac{1}{2}$  to 1 hr. the alk. soln. is sepd., the benzene allowed to percolate through silica gel and then distd., giving an approx. 90% benzene which was used in the engine tests. For results of the tests see C. A. 17, 3770.

W. W. HODGE

**Measurement of the relative absorption efficiencies of gas-absorbent oils.** R. E. WILSON and H. S. DAVIS. *Ind. Eng. Chem.* 15, 947-50 (1923).—The relative absorption efficiencies for benzene of 8 gas-absorbent oils (7 petroleum oils and 1 coal-tar oil) were measured by 2 different vapor-tension methods (C. A. 17, 2951, Davis and Davis, C. A. 17, 3811). The 7 petroleum oils, which varied considerably in boiling range and method of production, absorbed substantially the same % vol. of benzene (4.13 to 4.38), while the coal-tar oil absorbed 5.64, but its objectionable properties detract from its use in com. installations. The differences in mol. wt. of the oils should have produced variations in absorption efficiencies if Raoult's law held, but it was found that these differences were practically counterbalanced by the deviations from



this law. In the light of the results, it does not appear necessary to prescribe any absorption or vapor-pressure test for gas-absorbent oils of the ordinary range of composition.

J. L. WILEY

**Quantity and nature of gas from anthracites heated in vacuum.** P. LEBEAU. *Compt. rend.* 177, 456-8(1923).—Additional data on previous work (cf. C. A. 17, 3411) are presented, giving values for gas volumes obtained by distn. of 1-g. samples at 1000° and 1200°, volatile matter, moisture and ash, for anthracites from (1) Saint Martin-de-Valgalgues, (2) La Mure and (3) Pays de Galles. The gases averaged about 90% H<sub>2</sub>, 1-5% CO<sub>2</sub>, 1-2% CO. Little CH<sub>4</sub> or its homologs and no olefins were found. L. holds the vol. of the gas obtained from carbonization of solid fuels is not a function of the volatile matter of the fuel. The H<sub>2</sub> content is considered important, being a potential source of H<sub>2</sub> for NH<sub>3</sub> synthesis.

R. L. BROWN

**Making gas by the backrun process.** GEO. E. WHITWELL AND D. J. YOUNG. *Chem. Met. Eng.* 29, 664-9(1923); cf. Klyce, C. A. 17, 3775.—The Young-Whitwell backrun gas process has been in operation 2 yrs. It is applicable to any existing water-gas set with slight modifications. An exposition of principles and practice as based upon actual com. operation is given.

J. L. WILEY

**Low-temperature carbonization.** V. Z. CARACRISTI. *Power* 57, 831-6; *Am. Gas J.* 119, 65-9, 76-8(1923); cf. Morgan, C. A. 17, 2182.—The Caracristi-Piron lead-bath process, as developed for the Ford Motor Co., consists essentially of horizontal firebrick retorts, 44 to 52 ft. long, having 2 horizontal arched chambers 14 ft. wide and 6 ft. 5 in. high, with curtain walls at each side to sep. the heating and exhaust chambers from the distn. space. These chambers are connected by cast-Fe U-shaped flues in twin form, the lower section of the flues being completely submerged in a bath of molten Pb contained in a tank built of refractory brick. The heating gas is burned by downward combustion in refractory flues on both sides of the tank above the surface of the molten Pb, the hot combustion products being passed through the bath by means of the U flues. In each chamber is a flat conveyor made of cast-Fe plates riding upon the surface of the molten Pb. The raw coal is pulverized and travels through the heating chamber as a thin layer 1/2 in. thick and is carbonized in about 5 mins. at a temp. of 1000° to 1200°. Pb has been found to be ideal as the heat-transfer and conveyor-floating medium on account of its high sp. gr., low m. p., high b. p., freedom from affinity for extraneous elements, except free O which, however, does not exist in the atm. in which it works, and being unaffected by S at the temps. used. The power required to drive the mechanism is about 3/4 kw. hr. per ton of output. A heat balance gives the total heat requirements per lb. of coal as 428 B. t. u. The thermal efficiency of the process will be 95.7%. The coke obtained has all the qualities of low-temp. coke and forms a most desirable smokeless fuel.

J. L. WILEY

**Potentialities of low-temperature distillation in the conservation of our fuel resources.** V. Z. CARACRISTI. *Chem. Age (N. Y.)* 31, 361-5(1923); cf. preceding abstr.—The Caracristi-Piron lead-bath process is referred to. The com. justification for low-temp. distn. plants lies primarily in the material increase in market value of the products. Using as a basis 36% volatile coal at \$3.00 per ton, the coke produced costs \$4.46 per ton, including all operating and fixed charges as well as the shrinkage in the wt. of the coal during the process. Approx. 1 1/2 tons of coal will be necessary to produce 1 ton of coke. Further products are: 9300 cu. ft. of gas suitable for domestic use costing 7.5 cents per 1000 cu. ft.; 33 gal. heavy oil costing 1.5 cents per gal.; 26 lbs. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> costing 2 cents per lb.; 7 gal. light oil suitable as gasoline substitute costing 7.3 cents per gal. The 33 gal. of heavy oil can be redist. yielding: 6 gal. of gasoline substitute costing 6 cents per gal.; 4 gal. creosote oil for use as wood preservative costing 7 cents per gal.; 13 gal. heavy fuel oil costing 3.5 cents per gal. Coals suitable for low-temp. distn. range from bituminous to peat. Low-temp. distn. can also be applied to the distn. of wood, to the recovery of petroleum from shale, to central power plant practice and to the factory power plant.

J. L. WILEY

**Determination of light oil with activated carbon.** R. KATTWINKEL. *Chem.-Ztg.* 47, 682-4(1923).—Coke-oven gas is passed through a cold satd. soln. of picric acid, cotton wool filter, granulated CaCl<sub>2</sub>, activated C and a gas meter. 100 g. of C are used in a cylinder 40 × 140 mm. Light oil is driven off by direct steam superheated to 300° and read after condensing in a graduate. The same steam first passes around the adsorption cylinder for external heating. The moisture content of the C after the process is about 7%. Satisfactorily checking results are obtained with quantities of 0.2 to 3 m.<sup>3</sup> gas at a max. rate of flow of about 200 l. per hr. No influence of gas velocity upon absorption could be observed.

B. J. C. VAN DER HORVEN

**The determination of benzene in gas by means of active charcoal.** A. KRIEGER

*Chem.-Ztg.* 47, 357-8(1923).—Further study of the active-charcoal method for detg.  $C_6H_4$  in gas (cf. *C. A.* 16, 2771) has shown it to be less generally applicable than hoped for. The activity of the charcoal diminishes under various conditions and a satisfactory method for prolonging its activation and the correct temps. to prevent adsorption of condensed steam are yet to be detd.

C. C. DAVIS

**Indene and styrene: constituents of carburetted water-gas tar.** R. L. BROWN AND R. D. HOWARD. *Ind. Eng. Chem.* 15, 1147(1923).—Indene *A* and styrene *B* were isolated and identified as constituents of carburetted water-gas tar, *A* through its oxybromide, m.  $130^\circ$ , *B* through its dibromide, m.  $73^\circ$ . *A* was found present in 1.2 to 1.9% and *B*, 0.7 to 0.9% in the tars examd.

R. L. BROWN

**Water-gas tar emulsions.** W. W. ODELL. *Bur. Mines, Tech. Paper* 304, 51 pp. (1923); cf. *C. A.* 16, 1656.—Points not covered in the abstract of the preliminary report are: In the present systems of cooling carburetted water-gas and condensing the liquid products therefrom, it is natural that emulsions, either stable or weak, should form in the normal operation of a gas works. The stability of these emulsions increases as the completeness of oil cracking decreases. The primary causes for incomplete cracking of oil in the production of water-gas are low temp. in the checker chambers, dirty (C-coated) checker brick, insufficient time of contact of the oil with the checker brick, changing the oil without altering other variables to suit, and unsuitable spray nozzles. The relative completeness of cracking in one set of a number can be detd. by testing the tars. Although tars with sp. gr. approx. 1.00 tend more readily to form stable emulsions, it is evident that low sp. gr. merely indicates a high content of paraffins or other chem. difficulties which cause emulsion formation and is in itself not a primary cause of emulsion troubles. Too sudden cooling of the gas is to be avoided as tending to increase emulsion formation, as well as the use of a large excess of steam in gas making on account of its cooling effect in the cracking chambers. Collecting all condensates of tar and water in a common well or sepg. tank may aggravate emulsion troubles.

J. J. MORGAN

**Viscosity of coke-oven tars and soft pitches.** W. J. HUFF. *Ind. Eng. Chem.* 15, 1026-30(1923).—Presents new data on the change with temp. of the viscosity of typical coke-oven tars and soft pitches in such units as may be applied directly in the calcn. of the pressure drop in pipe lines. Directions and formulas which cannot be abstracted briefly are given. These data are valuable in the design of pumps, piping and burners for the use of these substances.

J. J. MORGAN

**The burning point and combustibility of cokes.** K. BUNTE. *Brennstoff-Chem.* 4, 167-8(1923).—The combustibility of various cokes may be judged by the results of the burning-point test. This test is carried out in an elec. furnace on finely divided coke and in a current of air of definite velocity. The burning temp. of a coke is considered as the point at which the temp. of the coke suddenly rises above that of the elec. furnace.

C. T. WHITE

**Possibility of using chlorosulfonic acid for the adsorption of ethylene from gaseous mixtures (TRAUBE, JUSTH) 10.** Vertical and lateral variations in the composition of bituminous coal seams (BRIGGS) 8. The nature of the processes of ulmification and of coal formation (PAGE) 8. Separation of gas mixtures (SHEPHERD, PORTER) 1. Ammoniacal liquor for softening water (CHEVALER) 14.

**Motor fuel.** J. M. A. CHEVALIER, P. BOURCET and H. REGNAULT. U. S. 1,469,148, Sept. 25. "Volatile oil of resin" is mixed with alc. and light acetone oil. Cf. *C. A.* 16, 334.

**Motor fuel.** W. T. SCHREIBER. U. S. 1,469,053, Sept. 25. A fuel for internal-combustion engines is formed of kerosene and gasoline or a similar petroleum distillate, diethyl ketone and alc., with or without ether or acetone or  $C_6H_6$ . Cf. *C. A.* 16, 3384.

**Condensing casing-head gas.** G. E. GRAY. U. S. 1,470,116, Oct. 9. Casing-head gas is introduced into a receptacle contg. cooled layers of metal wool or other finely divided metallic contact substance, condensate is drained off and uncondensed gas is led from the top of the receptacle into a second similar receptacle and sprayed with a liquid hydrocarbon.

**Gas producer.** F. H. TREAT. U. S. 1,469,399, Oct. 2.

**Diaphragm for gas meters.** C. P. DUBBS. U. S. 1,470,352, Oct. 9. Diaphragms are formed of leather or other non-metallic material impregnated with oil to give it flexibility and faced with goldbeater's skin to prevent solvents in the gas from attacking the oil in the body portion of the diaphragm.

**Coking retort oven.** J. VAN ACKEREN. U. S. 1,469,491, Oct. 2.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Centrifuging petroleum emulsions.** E. E. AYRES, JR. *Trans. Am. Inst. Mining Met. Eng.* No. 1276, 9 pp. (1923); *Oil & Gas J.* 22, No. 20, 58, 88-92; *Nat. Petr. News* 15, No. 41, 32C, 32D, 32E.—Centrifugal force and gravity have 2 distinct functions; (1) subsidence, in which the suspended globules are brought into contact; and (2) coalescence, in which the films around the globules are ruptured. In a water-in-oil emulsion subsidence would yield oil, free or nearly so of water, and a coned. water-in-oil emulsion. An exercise of both functions would yield an oil-free water. Centrifugal force is better than gravity for subsidence, but only slightly better for coalescence. Application of centrifuging to bottom settlings accumulations, crude oil-salt water emulsions, acid sludge in oil, emulsions of sour oils and water, etc., are discussed. D. F. BROWN

**Centrifuging removal of wax from all lubricating stocks.** L. D. JONES. *Trans. Am. Inst. Mining Met. Eng.* No. 1275, 5 pp. (1923); *Oil & Gas J.* 22, No. 20, 92-6; *Nat. Petr. News* 15, No. 41, 32A, 32B.—Early methods of centrifugal application are described as well as the more recent developments. The effectiveness of the centrifuge in removing wax from the chilled oil is entirely dependent on the manner in which the dild. oil is chilled. The most satisfactory method is to use a tank provided with brine-circulating coils as a container for the oil mixt. The coils extend from top to bottom of the tank and are either grouped at the center of the tank, or extend around the wall, leaving the center clear. The oil mixt. is heated to about 100° F. until all wax is in soln. and all the moisture has settled out. The mixt. then becomes bright and is transferred to the chilling tank. Brine at not more than 10° F. lower temp. than the oil is circulated through the coils. This gives a cooling rate of about 3° F. per hr. Every hr. the oil in the tank is turned over by a slowly moving agitator, insuring equal distribution of temp. and pptd. wax. Chilling is continued to about -10° F. Centrifuging at that temp. will produce a bright stock of 15° F. cold test from most crudes. Three conditions must be fulfilled in the dild. of the cylinder stock. The viscosity must be sufficiently reduced to permit crystal formation rather than colloidal pptn., and to permit the removal of the wax after it has pptd. The density of the mixt. must be reduced below that of the wax. Sufficient vol. of liquid must be provided for free suspension of the pptd. wax. Centrifugal sepn. gave a yield of 85% of 15° F. cold test bright stock as compared with the usual yield of 70% of bright stock of cold test 50° F. obtained by the cold settling process. D. F. BROWN

**Reclamation of used petroleum lubricating oils.** W. H. HERSCHEL AND A. H. ANDERSON. *Bur. Standards, Tech. Paper No. 223*, 93-108 (1922).—Used lubricating oils may be reclaimed by app. already commercially available and thus saved for further use. Such reclaimed oils will pass all the commonly accepted tests for new oils, such as flash point, viscosity, and sediment. It is more doubtful whether the reclamation process sufficiently reduces the org. acidity and S content, but there is some doubt whether this is necessary. There is little possibility that the org. acidity would ever be high enough in an uncompounded oil to cause corrosion. High acidity is often accompanied by readiness of emulsification, but exceptions have been found, so that the value of the test for acidity must lie in the possibility that an oil of high acidity will not prove durable in use. When more is known concerning the best test for durability of an oil, it may be necessary to modify reclaiming methods so that reclaimed oils may meet such test. E. H. LESLIE

**Petroleum asphalts in the roofing and waterproofing industries.** D. FINLEY. *Chem. Met. Eng.* 27, 798-803 (1922).—The history of the development of asphaltic roofing and waterproofing materials is given. The California asphalts of the 80's were the first used to be followed by the oxidized asphaltic products as made by Byerly from Eastern petroleum residues. The roofings of to-day are built on bases of rag felt, asbestos felt, or paper felt. The application of these products to roofing and waterproofing is described. Building papers, asphaltic paints, natural asphalts, and coal-tar pitches are briefly discussed. E. H. LESLIE

**Detection of pine oil in oil of turpentine.** HANS WOLFF. *Z. anorg. Chem.* 36, 233 (1923).—A reaction of pine oil described previously by W. (cf. *Farben-Ztg.* 17, No. 2) is utilized as a sensitive simple and cheap method for detecting the adulteration of oil of turpentine with pine oil. Four cc. of a mixt. of equal parts of 0.2%  $K_4Fe(CN)_6$  and 0.04%  $FeCl_3$  solns. are shaken with 3-5 drops of the sample. An intense blue color or a ppt. of Prussian blue rapidly appears if pine oil is present. Oil of turpentine gives only

a greenish color or a slight blue color at the boundary of oil and  $H_2O$ . It is not necessary to distil the oil first, even when old.  
C. C. DAVIS

Oil-yielding rocks in the Union of S. Africa (TREVOR) 8. The constituents of wood spirit oil (PRINGSHEIM, LEIBOWITZ) 10.

**Distilling oil shale.** R. C. DUNDAS and R. T. HOWES. U. S. 1,469,628, Oct. 2. A charge of oil shale is slowly and progressively burned in a closed chamber from the top downwardly while the temp. of combustion is maintained substantially const. by regulation of a downward current of air through the chamber. Hydrocarbon products are drawn off at the bottom of the chamber.

**Apparatus for cracking oil.** G. EGLOFF and H. P. BENNER. U. S. 1,470,353, Oct. 9. Oil passes through a coil in a heating chamber and this coil connects with a vapor chamber with a plurality of outlets from its different portions. Each of these outlets leads to a dephlegmating device and drawoff lines lead from the dephlegmators to a common header. A vapor outlet extends from the header and devices are provided for cutting off the drawoff lines as desired.

**Removing carbon from metal pipes in oil-cracking apparatus.** C. J. GREENSTREET. U. S. 1,470,359, Oct. 9. O and steam are passed simultaneously through pipes contg. C while heated sufficiently to cause oxidation of the C.

**Reclaiming waste lubricating oil.** J. R. MILLER. U. S. 1,469,426, Oct. 2. Waste lubricating oil from gasoline engines is heated and steam is injected into the oil to sep. its particles and expel volatile substances. A soap soln. is added and the oil further treated with steam to coagulate dirt and  $H_2O$  and solid substances are sep'd. from the oil.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**Partial hydrolysis of white spruce cellulose.** E. C. SHERRARD and G. W. BLANCO. *Ind. Eng. Chem.* 15, 1166-7(1923).—By the extn. of cellulose prep'd. from spruce wood by the Cross and Bevan method, by prolonged boiling with  $H_2O$  and evapn. the ext. to a thick sirup, a white powder is obtained by pptn. with EtOH. This powder is very sol. in  $H_2O$ , has a small reducing value and gives no test for mannose. By hydrolysis with dil. acids the reducing value is increased 5 times and a test for mannose is obtained. The powder darkens at  $220^\circ$ , is insol. in EtOH,  $CHCl_3$ ,  $Me_2CO$ ,  $MeOH$  and  $C_2H_5$  and shows no reaction with  $PhNHNH_2$ .  
FRANCIS G. RAWLING

**Many applications of sodium silicate suggested by its uses in the paper mill.** J. G. VAIL. *Chem. Met. Eng.* 29, 621-2(1923); cf. *C. A.* 16, 492. —**Acid-proof cement** is made from  $Na_2O \cdot 2.4SiO_2$ , quartz, and port. cement. Higher ratio silicates are used in **hardening concrete**, as **adhesives**, for **coating** paper to render it grease-resistant, and as **sizing agents**. Clay is rendered more fluid and is retained to a greater extent when Na silicate is present in the beater.  $Na_2O \cdot 2SiO_2$  is used as a **boiler compd.** Also in *Oil, Paint, Drug Rep.*; *Paper* 32, No. 25, 7-8; *Paper Trade J.* 77, No. 12, 46-7; and *Paper Ind.* 5, 1113-4.  
WM. STERICKER

**Recommended specification for limestone and quicklime for use in the manufacture of sulfite pulp.** ANON. Bur. Standards, *Circ.* 144 (July 6, 1923).—The specifications cover limestones high in Ca and Mg and quicklime on a basis of 95% purity. Requirements of quality, compn., allowable impurities, sampling and testing methods, etc., are included.  
C. E. CURRAN

**Behavior of bag paper at  $80^\circ$ .** W. HERZBERG. *Wochbl. Papierfabr.* 54, 2059-60 (1923).—The results are tabulated of several tests on paper bags used for holding cement at temps. between  $60$  and  $80^\circ$ . After drying for 5 hrs. at  $80^\circ$  the paper contained only 15% of its original moisture, the tearing strength was greater, the  $\epsilon$ , stretch smaller, and the folding endurance decreased to about 1% of the original. A subsequent 24-hr. seasoning, at 65% humidity, brought all the values close to normal. The few tests demonstrated that paper heated to  $80^\circ$  becomes brittle and until it has absorbed sufficient moisture it is sensitive to mech. treatment.  
J. L. PARKSONS

**Simple paper-testing procedure.** W. HERZBERG. *Mitt. Materialprüfungsamt* 9, (1922); *Papierfabr.* 21, 343-6(1923); *Wochbl. Papierfabr.* 54, 2104-5(1923).—The following 10 tests for paper, which are easily carried out without special app. or knowledge, are described briefly: resistance to crumbling and rubbing, thickness, wts. per sq. m.

and per cu. dm., ash, ground wood detection, sizing, sunlight, resistance to grease or oil, and distinction between genuine and imitation parchment. J. L. PARSONS

**The influence of atmospheric moisture on paper.** G. SCHINKEL. *Wochbl. Papierfabr.* 54, 2268-72(1923).—When paper absorbs moisture 2 kinds of phenomena occur: a swelling of the fibers, and a contraction of the sheet. With moist paper under pressure, the contraction changes to expansion under certain conditions. The chief requirements for paper storage are that the atm. moisture and temp. be as nearly const. as possible. Data are given from the expts. with 12 paper samples in the form of disks exposed to humidities of 96, 85, and 70%. The surface changes with paper made from chem. pulp are greater than that made from mech. pulp. J. L. PARSONS

**The Rinman process.** E. HEUSER. *Papierfabr.* 21, 325-30(1923).—An address covering the development and use of the Rinman process in Germany. The av. yield of by-products per ton of pulp are: pure MeOH 10 kg., pure Me<sub>2</sub>CO 8 kg., MeEtCO 10 kg., higher ketones 6 kg., light oils 4 kg., and heavy oil 32 kg. J. L. PARSONS

**The constituents of pulp wood.** R. SIEBER. *Papierfabr.* 21, 317-21(1923).—An address in which elaboration is made on the theme that wood consists mainly of carbohydrates existing in all degrees of polymerization with consequent varying ease of hydrolysis. Lignin is probably a cyclic compd. J. L. PARSONS

**The probable reasons for the strength of kraft paper.** ANON. *Papierfabr. (Fest u. Aus. Hef)* 21, 60-2(1923).—Not only do the resins contribute to the strength of kraft paper but also the fatty constituents of the pulp. These probably contain unsatd. acids, which at an elevated temp. are oxidized and form polymerized films in the paper, thus knitting the fibers together. Old trees do not yield these substances to such a degree as young ones. The possibility of utilizing the fresh extract of conifers for sizing paper is suggested. J. L. PARSONS

**Gas absorption by paper.** P. KLEMM. *Wochbl. Papierfabr.* 54, 1515-18(1923).—Yellowing of paper is due usually to the O of the air; other contributing factors are light and temp. It may also be due to gaseous N compds. formed when paper is sized with casein. The reddening of sulfite pulp may be the result of oxidation of colorless compds. formed in the cooking process. PhOH and PhNH<sub>2</sub> vapors produce noticeable effects; PhNH<sub>2</sub> in printing ink often causes printing to appear on the reverse side of the sheet. Rosin-sized paper deteriorates on exposure to light, while paper contg. both rosin and starch does not break down so readily. Extreme heat is to be avoided in drying. J. L. PARSONS

**Composition of different straws and the pulps resulting from them by different processes.** TH. F. BLASWEILER. *Papierfabr.* 21, 309-11, 321-2, 361-5, 373-6(1923).—The compn. of oat straw is given as 45.49% cellulose, 24.70% pentosan, and 29.81% lignin, on the dry and ash-free basis. The corresponding values for rye straw are 42.83, 26.65, 30.52, and for rape straw 32.09, 25.52, and 42.39. Oat husks contain less cellulose and more pentosans and lignin. Comparative digestion expts. were carried out with NaOH, CaO, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S, and NaHSO<sub>3</sub>. The tests with NaOH included treatments under pressure, in an open vessel, by Steffen's method, and according to Beckmann in the cold. In general the NaOH effected the best soln. of the incrustations. The lignin resisted the action of most of the chemicals but the pentosans were dissolved. Numerous data are listed in tabular form. J. L. PARSONS

**Comparative bleaching experiments with chlorine gas and bleaching powder.** E. HEUSER and W. NIETHAMMER. *Papierfabr. (Fest u. Aus. Hef)* 21, 52-60(1923).—Comparative bleaching expts. were carried out at room temp. on a Ritter-Kellner sulfite pulp having a Cu no. 2.20. Upon bleaching to a standard white, in the usual way with bleaching powder for 6 hrs., the Cl consumption amounted to 3.2%, the Cu no. increased to 3.13, and the yield was 96.5%. Cl gas was next passed through a suspension of pulp in water for an hr. but a full white was not obtained. In this expt. the Cl consumption varied from 2.5 to 2.9%, independently of the quantity of gas passed through; the max. Cu no. was 2.90, and the yield was 97%. A combined Cl gas-bleaching powder bleach gave the best results. After treating the pulp mixt. with Cl gas, which amounted to 62-72% of the total requirement, the pulp was washed with H<sub>2</sub>O or 1% NaOH soln. To obtain the same degree of whiteness, as by a single bleaching process, only about 50% of the Cl was required and the time was shortened to 80 min.; the Cu no. was lower, 1.9; and the yield was higher, 97.5-98.1%. Washing the pulp with 1% NaOH soln. gave better results than using H<sub>2</sub>O alone, thereby effecting a Cl saving of 45-54% compared to the usual process with bleaching powder. J. L. PARSONS

Cellulose chemistry (HIBBERT, TRIMM) 10. Action of chloral on cellulose (ROSS, PATNE) 10.

**Alkali cellulose.** P. C. SEEL. U. S. 1,469,824, Oct. 9. Pulverulent, intimately mixed alkali cellulose suitable for etherification is obtained by compacting NaOH, cellulose and H<sub>2</sub>O into a dense layer, breaking the layer up into fragments and grinding the fragments to powder.

**Cellulose ether composition.** I. C. MATTHEWS. U. S. 1,469,816, Oct. 9. A compn. adapted for making films is formed of cellulose ethyl ether dissolved in a mixt. of C<sub>6</sub>H<sub>6</sub> and  $\beta$ -chloroethyl acetate.

**Cellulose ether composition.** W. R. WEBB. U. S. 1,469,862, Oct. 9. A compn. adapted for forming films is prepd. from cellulose ethyl ether dissolved in a mixt. of Et benzoate and MeOH, EtOH or other lower alc. U. S. 1,469,863 specifies a compn. contg. cellulose ethyl ether and benzyl acetate, with or without other ingredients such as MeOH or camphor.

**Cellulose ether composition.** P. C. SEEL. U. S. 1,469,825, Oct. 9. A compn. adapted for forming films is made from cellulose ethyl ether dissolved in a mixt. of BuOAc 25 and MeOH 75 parts. U. S. 1,469,826 specifies a compn. of cellulose ethyl ether dissolved in a mixt. of mesityl oxide, MeOAc and MeOH.

**Cellulose ether composition.** S. J. CARROLL. U. S. 1,469,812, Oct. 9. Acetone oil (or similar ketonic material) is used with cellulose ether (*e. g.*, Et ether), with or without other ingredients such as MeOH, EtOH, triphenylphosphate or camphor to prep. a compn. adapted for making films. U. S. 1,469,813 specifies a compn. formed of cellulose ethyl ether dissolved in a mixt. of Me benzoate with ales. and other ingredients.

**Bleaching cellulosic material.** E. EBLE and G. A. RICHTER. U. S. 1,470,556, Oct. 9. Sulfite pulp or similar material after preliminary bleaching which may be effected by an alk. hypochlorite is subjected to a further "super-bleaching" with Cl to effect additional whitening without any substantial change in the strength or beating qualities of the material.

**Films and filaments from cellulose acetate.** C. W. PALMER and W. A. DICKIE. U. S. 1,465,994, Aug. 28. Films or filaments are formed from a soln. of cellulose acetate in acetone forced through an orifice into a coagulating bath contg. NH<sub>4</sub>CNS, which serves to strengthen the filaments formed so that they can be drawn to a fineness as great as 1 • 2 deniers. The thiocyanate is removed from the product by washing and the purified translucent threads are dried. NaCNS, KCNS or Ca(CNS)<sub>2</sub> also may be used to effect swelling and control coagulation. Benzyl alc. may be used with the acetone cellulose acetate compn. as a plasticizing agent. Cf. C. A. 17, 3789.

**Composite films.** F. W. LOVEJOY. U. S. 1,469,815, Oct. 9. Strips of cellulose nitrate or acetate or similar cellulosic compns. are caused to unite at their edges while contg. sufficient volatile solvent to effect their union. Composite strips thus united may be used for motion picture films.

**Treating black liquor from sulfate pulp manufacture.** G. A. RICHTER and D. H. McMurtrie. U. S. 1,469,960, Oct. 9. See Can. 232,746 (C. A. 17, 2956).

**Flexible sheets of pyroxylin.** W. G. LINDSAY. U. S. 1,468,820, Sept. 25. Flexible sheets are shaved from a block of rubber-like consistency formed of nitrocellulose and tricresyl phosphate.

**Bleaching paper pulp.** J. C. BAKER. U. S. 1,468,693, Sept. 25. Paper pulp is subjected to the action of a Cl-contg. bleaching agent such as CaOCl<sub>2</sub> until bleaching is nearly completed and the remaining Cl-bearing material is then neutralized or destroyed, and the pulp is acidified, *e. g.*, with SO<sub>2</sub>, which performs both of these functions. Cf. C. A. 16, 2224.

**Composition for imparting translucency to paper.** S. H. PARRISH. U. S. 1,468,831, Sept. 25. Soy-bean oil 1 is mixed with CCl<sub>4</sub> 3 parts and this soln. is then mixed with another soln. formed from fir balsam 8 and turpentine 4 parts. Cf. C. A. 16, 2780.

**Waterproof paper board.** A. L. CLAPP. U. S. 1,468,959, Sept. 25. Finely divided Montan wax is beaten into a pulpy mass of cellulose fiber contg. finely divided Ca(OH)<sub>2</sub> and a pptg. agent such as alum is added. The material is formed into sheets which have an exterior layer of the waterproofing material not exceeding 0.002-0.003 in. in thickness.

## 24—EXPLOSIVES AND EXPLOSIONS

C. E. MUNROE

**The transportation of explosives in and about mines.** L. C. ILSLEY. U. S. Bur. of Mines. *Repts. of Investigations* No. 2528, 8 pp. (1923).—State regulations are given and discussed. E. J. C.

**Strength and sensitiveness of TNT as determined by the laboratory "sand-test" bomb.** C. A. TAYLOR AND R. D. LEITCH. Bur. of Mines, *Repts. of Investigations* No. 2526, 5 pp. (Sept. 1923).—TNT was purified by 8 different methods, while the most highly purified, setting point 80.6°, was comminuted to 9 different degrees, by crystn. from various solvents under differing conditions of cooling, or by fusion and grinding, and portions of each were fired in the sand-test bomb. The sensitiveness and efficiency varied directly with the purity. From a given solvent the fine crystals were slightly the more sensitive. Fusion decreased both the strength and sensitiveness unless the TNT was crushed fine. Results from tests of these samples repeated after 2 yrs. checked as did tests made in 1915, 1921 and 1923 on 2 other samples, indicating that TNT stored in the dark does not change.

CHARLES E. MUNROE

**Wave distribution at the Alum Chine explosion.** C. E. MUNROE. *Army Ordnance* 4, 94-7(1923).—Describes the circumstances attending the explosion on board the S. S. Alum Chine in Balt. harbor, Mar. 7, 1913, while being loaded with 600,000 lbs. of frozen dynamite. A chart is given of localities, as far distant as 104 miles to the east, where effects were noted.

CHARLES E. MUNROE

**Oxygen-oil explosions. Preliminary report. II. Spontaneous ignition of metals in oxygen under pressure.** J. J. JAKOWSKY AND E. W. BUTZLER. Bur. Mines, *Repts. of Investigations*, No. 2521, 4 pp., 2 plates(1923).—The ignition point of the metals tested in O fell as the pressure increased. Fe in O at atm. pressure ignited at 930° while at 2000 lbs. per sq. in. it ignited at 600°, which is below its m. p. Under high O pressures Fe and steel burn very rapidly and completely and when ignited propagate flame with almost explosive velocity. Brass and Cu behave much alike and differ considerably from Fe in that their m. ps. are below their ignition pts. as is that of Pb. The rapidity of combustion of a substance in high-pressure O appears to be influenced by its heat of combustion and its thermal cond., for the higher the former and the lower the latter the greater the rapidity of its combustion. It is indicated that it may be unsafe to use Fe manifolds, pipes, etc., for compressed O while if made of Cu or, perhaps, brass they would survive a higher temp. than steel, and when they reached their m. ps. they would melt and release the O without burning or propagating flame.

CHARLES E. MUNROE

Temperature of explosion for endothermic substances (DATTA, *et al.*) 10.

**Explosive priming composition.** H. RATHSBURG. U. S. 1,470,104, Oct. 9. Primers are charged with the Pb salt of trinitrophenylglucitol which is inert to Al, brass and Cu and not affected by atm. humidity. Cf. C. A. 17, 3101.

**Oxalic acid from fulminate waste liquors.** E. A. BARNES. U. S. 1,468,792, Sept. 25. Waste residual liquor from the manuf. of Hg fulminate is evapd. to a sp. gr. of about 1.20, the glycolic acid is oxidized by this operation and the oxalic acid formed is crystd. on cooling.

**Carbon cartridge for explosive use with liquid oxygen.** A. MESSER. U. S. 1,469,442, Oct. 2. The cartridge is adapted for use as an initial igniter.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**The ionamines: a new class of dyestuffs for acetate silk.** A. G. GREEN AND K. H. SAUNDERS. *J. Soc. Dyers Colourists* 39, 10-6(1923).—Acetate silk lacks affinity for direct as well as most of the acid dyes. It has an affinity for some basic dyes, especially in the presence of inorg. salts such as  $MgCl_2$ ,  $NaCl$  or  $ZnCl_2$ ; for certain hydroxy-azo dyes contg. no sulfonic groups, such as *p*-nitroanilineazosalicylic acid (alizant yellow R), and picramic acid azo-*m*-phenylenediamine (metachrome brown B); and for aminoazo bases in soln. or suspension, which may be subsequently developed upon the fiber. It was thought that dyes contg. hydroxyalkyl radicals attached to N might, by virtue of their alc. groups, possess affinity for acetylcellulose. A number of azo compds. including  $H_2NC_6H_4N:NC_6H_4N(C_2H_4OH)_2$ ,  $O_2NC_6H_4N:NC_6H_4N(C_2H_4OH)_2$  and  $PhN:NC_6H_4N(CH_2CH(OH)CH_2OH)_2$ , were prepd. Although the simpler bases had on account of their soly. in  $H_2O$  an affinity for acetyl silk, this affinity diminished as the number of alc. groups increased. From this it appeared that the dyeing of acetyl silk is mainly a soln. phenomenon for which the following conditions are necessary: (1) The dyestuff should contain amino-, substituted amino-, or hydroxyl groups; strong

salt-forming groups, such as the sulfonic group, should be absent. (2) When basic compds. are employed as their salts with acids, such as hydrochlorides of dye bases, the salt must be readily dissociated by  $H_2O$ , as it is the base and not the salt which the fiber absorbs. (3) This free base should be sparingly sol. in  $H_2O$ . (4) As high mol. complexity tends to diminish soly. in non-aq. solvents (fiber), the mol. should not be too large. These theories led to the  $\omega$ -sulfonic acids of amino compds. contg. the group  $NR'CHR''SO_3H$ , in which  $R'$  and  $R''$  are alkyl groups or  $H$ , e. g.,  $PhN:NC_6H_4NHCH_2SO_3H$ . Certain of these compds. are readily hydrolyzed by dil. acids or alkalis, but are fairly stable in neutral soln. Such azo compds., ionamines, which were sol. in  $H_2O$ , behaved generally like ordinary acid dyes and readily dyed acetate silk from a slightly acidified or alk. bath at 65–75°. The fiber contg. the free aminoazo base could be diazotized and coupled with unsulfonated phenols and amines. In this manner light and heavy shades were produced varying from orange to scarlet, red, maroon, violet, blue and black. The compds. produced from secondary amino compds. are not diazotizable but give direct shades. The dye penetrates, exhausts and levels well, and is fast to soaping, washing, rubbing, perspiration, etc. The ionamines which possess the highest affinity for acetate silk have no affinity for cotton, and *vice versa*. Wool is dyed by the unhydrolyzed ionamine as by an ordinary acid dye. Other varieties of artificial silk dye as cotton. Natural silk appears to be dyed partly by the hydrolyzed and partly by the unhydrolyzed dyestuff. The dyeing of acetate silk is explained on the soln. theory. The methods of dyeing, diazotization and development, and the dyeing of union materials are discussed.

CHAS. E. MULLIN

**Testing of dyes for fastness to light.** WM. T. ANDERSON, JR. *Textile Colorist* **45**, 576(1923).—A preliminary report pointing out the similarity to sunlight of the water-cooled quartz Hg arc lamp equipped with a suitable filter.

CHAS. E. MULLIN

**Influence of metallic hydroxides on the fastness to light of indigo.** R. HALLER. *Am. Dyestuff Rept.* **12**, 723–5(1923).—See *C. A.* **17**, 2365.

E. J. C.

**Cloudiness in chiffon hosiery.** ANON. *Textile World* **64**, 1799–1801(1923).—The cloudiness was not a dyeing defect but was caused by differences in fabric thickness due to wide variations in the no. of filaments and twist in the yarn.

C. E. MULLIN

**Skein silk dyeing.** H. R. TISDALE. *Am. Dyestuff Rept.* **12**, 697–702(1923).—Methods for removing the natural gum from the fiber, weighting silk, dyeing "pure dye," dyeing for fastness to washing, dyeing black, and souple dyeing are described.

L. W. RIGGS

**Dyeing of cotton goods.** J. STEPHEN HEUTHWAITE. *Am. Dyestuff Rept.* **12**, 719–22(1923).—Details are given for the dyeing of cotton with substantive colors.

L. W. RIGGS

**The evolution of bleaching.** S. H. HIGGINS. *J. Soc. Dyers Colourists* **39**, 265–70(1923).—A brief history of bleaching from the ancient Egyptians to the early part of the 19th century.

CHAS. E. MULLIN

**Electricity in bleaching cotton.** RAFFAELE SANSOME. *Textile World* **64**, 497–503, 1081–7, 1153–4(1923).—A discussion of the various methods of hypochlorite bleaching and their respective advantages. The use of nascent hypochlorite of low concn. is recommended.

CHAS. E. MULLIN

**Iron stains in cloth.** THOS. HADFIELD. *Textile World* **64**, 1527–9(1923).—Fe stains may be caused by its presence as an impurity in sizing materials such as  $CaCl_2$ ,  $ZnCl_2$ ,  $MgCl_2$ ,  $H_2O$  or clay. Where hygroscopic materials are used in sizing the stains may result from long contact with Fe machine parts, etc., or packing paper contg. Fe.

CHAS. E. MULLIN

**The newer ways with textile problems.** ANON. *Textile World* **64**, 1389–91, 1521–5, 1671–3(1923).—A review of some of the latest methods of making the various tests on fibers, yarns, fabrics, etc., as well as a description of the app. used and the applications of the data obtained.

CHAS. E. MULLIN

**Testing textile materials.** S. W. STRATTON. *Can. Colorist and Textile Processor* **3**, 200–5(1923).—A brief description of the methods used in the U. S. Bur. of Standards for testing textile materials, together with a list of the fees charged.

C. E. MULLIN

**Test methods for electrical yarns.** ANON. *Textile World* **64**, 1664–5(1923).—The proposed tentative methods of testing are given.

CHAS. E. MULLIN

**Quality of muslins and sheetings.** C. J. BURKLEY. *Textile World* **64**, 1673–7(1923).—The convenience of the Mullen tester for making a quick test on muslins and sheetings is pointed out. Comparisons are based upon an "index value" obtained by dividing the bursting strength of the fabric in lbs. per sq. in. by the wt. in oz. per sq. yd.

CHAS. E. MULLIN

**Action of light on cotton.** P. W. CUNLIFFE. *J. Text. Inst.* **14**, 314–8T(1923).—



A summary of the literature and of the findings of various observers of the action of light on cotton and in some cases on linen. L. W. RIGGS

Some bacteriological problems involved in the retting of flax. Z. N. WYANT. *Abstracts Bact.* 5, 208(1921).—The mineral content (type of salts and concn.) of the water is an important factor. The necessity to use pure cultures of bacteria for retting is uncertain. JOSEPH S. HEPBURN

Relation of the chemical and dyeing industries (MUSPRATT) 13. Dyes used in photography (MUNGILLO, GIBBS) 5. *p*-Nitrobenzeneazopyrogallol (Chrome brown P. A.)(JULLARD) 10. Quinoline derivatives; dyes (Brit. pat. 198,462) 10.

Indigoid vat dye. W. BAUER. U. S. 1,466,687, Sept. 4. Dichloroisatin is converted (in a dry  $C_6H_6$  suspension) into dichloroisatin  $\alpha$ -chloride by heating it with  $PCl_5$ . The mixt. thus obtained is then poured into a well stirred soln. of 6-methoxy-1-naphthol in dry  $C_6H_6$ . After stirring a short time, a dye seps. and is filtered off. It is a dark blue cryst. powder with a Cu-like luster; it yields with hyposulfite and NaOH a yellow vat, from which cotton is dyed a fast greenish blue. By treating the dye with chlorinating agents a black dye is obtained. From dibromo- $\beta$ -naphthisatin chloride and 6-methoxy-1-naphthol a product is obtained dyeing cotton from a hyposulfite vat fast olive-green.

Fabric impervious to acids and poisonous gases. C. D. ABRAHAM and G. L. SCHWARTZ. U. S. 1,468,791, Sept. 25. A fabric adapted for making laboratory gloves or other wearing apparel impervious to acids is prepd. by sewing sep. pieces of twill-weave cotton cloth or other textile material together and coating its exterior surface, including the seams, with a nitrocellulose compn. or other cellulose ester material.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

U. S. Government specification for gloss interior lithopone paint, white and light tints. Bur. of Standards, *Circ.* 147, 8 pp.(1923).—Standard specification No. 67. E. J. C.

U. S. Government specification for water-resisting red enamel. Bur. of Standards, *Circ.* 146, 6 pp.(1923).—Standard specification No. 66. B. J. C.

The effect of various pigments upon the rate of oxidation of linseed oil. F. H. RHODES and A. E. VAN WIRT. *Ind. Eng. Chem.* 15, 1135-40(1923).—The rate and amt. of O absorption by linseed oil paints contg. various white and inert pigments, was detd. by suspending the films in an atm. of O at const. temp. and pressure, and observing the vol. of O absorbed; the rate and amt. of volatile product evolution was calcd. from the wt. of the films and the known O absorption. The results support the hypothesis that the drying of linseed oil is an autocatalytic reaction, with the Pb salt present acting as a pseudo catalyst. Silica has little effect on the oxidation of the oil; leaded ZnO, lithopone, titanox, and BaSO<sub>4</sub> decrease the rate and amt. of oxidation and evolution of volatile matter; basic carbonate and basic sulfate white lead retard the initial oxidation of the oil, but increase the final amt. of O absorbed and volatile matter given off. Variable effects were observed with the same paint contg. ZnO. F. A. WERTZ

Moisture-resistant coatings for wood. FOREST PRODUCTS LAB. *Technical Notes* 181, 3 pp.(1923).—Shrinking, swelling, warping and checking of wood due to the absorption of moisture from the air can be prevented or retarded by proper coatings. Various coatings were tested but none was found that was entirely moisture-proof. Wood panels coated with 17 different materials either sep. or in combination were exposed to a humidity of 95-100% for 14 days and the amt. of water absorbed detd. The results of the expt. are summarized in a table expressed in percentage efficiency as compared with the untreated wood. Aluminium leaf on asphalt base shows the highest efficiency, 98%. The least efficient was linseed oil, 5 coats, 0.38%. Rubbing varnishes are more resistant to moisture than spar varnishes. ALFRED L. KAMMERER

Comments on linoleum treatment. H. A. GARDNER. *Paint Manufs. Assoc. of U. S.*, *Circ.* 138, 44-5(1923).—The practicability of protecting linoleum with varnish (see *Ibid.* *Circ.* 161, 99-101(Dec. 1922)) is sometimes interfered with by the presence of wax on the surface of the linoleum, which retards the drying of the varnish. Results of the examn. of linoleum waxes for residue and volatile matter are tabulated. F. A. WERTZ

**Printing ink.** G. W. HERBEIN. U. S. 1,469,414, Oct. 2. A vehicle, 65 parts, contg. fuel oil 86-95.5, rosin 1-10, Cu nitrate 0.5,  $\text{CaCl}_2$  1, NaOH 1 and Na silicate 1%, is mixed with Pb linoleate 4, pigment 25 and drier 6 parts, together with sufficient  $\text{H}_2\text{O}$  to permit reaction between the ingredients. The  $\text{H}_2\text{O}$  is afterward evapd.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

**The extraction of oil of seeds (of grapes) at Perpignan.** H. ASTRUC. *Rev. vit.* 39, 221-30(1923).—A description of a large scale process of extn. with a volatile solvent, trichloroethylene.

P. R. DAWSON

**Utilization of the fruits of *Melia azedarach* as a source of mangora oil.** E. DE WILDEMAN. *L'agr. coloniale, bull. mensuel jardin coloniale* 4, 74-7(1919); *Bull. Agr. Intelligence* 11, 588-9(1923).—The fruit of the Persian lilac or bead tree, *Melia azedarach*, yields mangora oil on expression. The seeds are rich in this oil; the pulp contains comparatively little oil. The oil melts at approx.  $35^\circ$ , and rapidly becomes rancid. It is used as an illuminant, in medicine, and in the manuf. of soap, paints, and varnishes.

JOSEPH S. HEPBURN

**Rendering animal fats.** J. LISTER. U. S. 1,470,228, Oct. 9. Stock to be rendered is subjected to the direct action of steam and allowed to settle while kept hot without diln. Hot undild. glue liquor is drawn off and the stock is again subjected to the direct action of steam; hot  $\text{H}_2\text{O}$  is added to float the tallow and the latter is skimmed off.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Deterioration of cut cane, juices, press cake, sirups and massecuites.** W. K. ORTH. *Intern. Sugar J.* 25, 474-8(1923).—Burnt cane showed an av. drop in purity of juice ranging from 0.3 in 2 days to 5.96 in 7 days. Such cane should be milled as soon as possible. Crusher juice deteriorates only slightly in 5 hrs., but last mill juice dropped 1.9 in purity in 30 min.; mixed juice as much as 0.5 in 1 hr. Ordinarily the deterioration of juice in transit from mill to heaters is not very great, but extreme cleanliness is necessary, as otherwise accumulations of trash in corners, etc., tend to destroy sucrose. Improved machinery and self-cleaners largely help to overcome this difficulty.  $\text{HCHO}$  is the best preservative,  $\text{Na}_2\text{CO}_3$  the least satisfactory. There is usually a slight destruction of sucrose in the settling tanks, either through prolonged heating, or, at lower temps., by microorganisms. When the juices are distinctly alk., an increase in purity may occur by destruction of invert sugar. There is no appreciable deterioration in the press cake, if the settlings are kept hot and alk., and very hot water is used, also made alk. if necessary. In sirups and pan-massecuites which are not distinctly acid, no sucrose is destroyed, but rather some invert sugar. There is no deterioration in crystallizers, but massecuites kept in tanks are liable to go back.

W. L. OWEN

**How chemical engineering helps the maker of cane sirup.** H. S. PAINE and R. S. McBRIDE. *Chem. Met. Eng.* 29, 702-5(1923).—To insure a high and uniform quality of com. cane sirup which will not cryst., the sirup produced by farmers is collected and treated in a plant of 5000-gallon capacity per 12-hr. day with an active invertase prepn. during 36 hrs., boiled to uniform d. in open pans, and canned after cooling to the process temp. Dark sirup may be decolorized with vegetable C and blended with light sirup. The cost of the invertase is 0.5¢ per gallon of finished sirup, and the total cost promises com. success. Illustrated with floor plan, side elevation of plant, and pictures.

F. W. ZERBAN

**The care and revivification of "Norit" decolorizing carbon.** J. N. A. SAUER. *Intern. Sugar J.* 25, 485-90(1923).—Fresh Norit can be purified by acid treatment, washing, and reburning. It must be kept free from dirt. Before it is stored dry, all sugar must be washed out; or else it may be stored wet by allowing it to ferment and washing afterwards. It can then be purified and reburned. In regular use it becomes contaminated with inorg. and org. impurities of various kinds. The latter, upon reburning, give rise to secondary C which can be removed by sifting, by treatment with acid and alkali, or by oxidation in the furnace with air, steam,  $\text{CO}_2$ , or CO under certain precautions. Revivification may, according to conditions, be effected by one or a

combination of the methods of acid treatment, alkali treatment, and reburning. The exact procedure for these 3 is described in detail. If 2 lbs. of Norit is used per 100 lbs. of sugar, and it is used 100 times, the cost is only 0.35 cents per 100 lbs. of sugar, and correspondingly more, if it is used fewer times. CaO must not be used for activating Norit, as it breaks down the C particles.

**Specificity in the forms of starch grains.** J. J. L. ZWIKKER. *Pharm. Weekblad* 60, 1109-17(1923).—A discussion of the literature. W. L. OWEN  
A. W. DOX

**Gum arabic solutions correctly prepared.** K. MICKSCH. *Papier-Zig.* 48, 1550 (1923).—Directions are given for making stable solns. of gum arabic. The addn. of Ca(OH)<sub>2</sub> prevents gelatinization and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> increases the cementing capacity of the soln. For cementing porcelain, glass, wood or paper 20 g. Ca(NO<sub>3</sub>)<sub>2</sub> are added to a mixt. of 200 g. gum arabic powder in 250 cc. H<sub>2</sub>O. J. L. PARSONS

Determination of the potash in cane juice as an indication of the fertilizer requirements of the soil (WALKER, GLICK) 15. Apparatus for filtering sugar solutions, etc. (U. S. pat. 1,469,026) 1.

## 29—LEATHER AND GLUE

ALLEN ROGERS

**The influence of hydrogen-ion concentration in the fixation of vegetable tannins by hide substance.** A. W. THOMAS AND MARGARET W. KELLY. *Ind. Eng. Chem.* 15, 1148-53(1923).—Expts. in tanning hide powder were made with exts. of gambier, quebracho, and hemlock, larch, oak, and wattle barks. Points of max. are found in all curves showing the rate of tanning as a function of concn. of total solid matter in soln. before tanning. The points of max. occurred at about the concns. at which the hide powder just completely detanned the solns. in the 24-hr. period. The rate of tanning varied markedly with change of  $p_H$  value. A point of max. occurs between  $p_H = 2$  and 3, a point of min. at 5, the isoelec. point of collagen, and a second point of max. at  $p_H = 7$  to 8, beyond which the curves fall steeply. The point of min., which is sharply defined when tanning for 24 hrs., becomes hardly noticeable after 2 weeks and disappears altogether after tanning for 21 weeks. The mechanism of tanning is discussed from the viewpoints of the phys.-chem. theories of Donnan, Procter, Wilson, and Loeb and of the oxidation theories of Meunier, Fahrion, and Powarnin.

**The color and dispersion of tanning materials.** G. GRASSER. *Z. Leder-Gerberie-Chem.* 2, 227-31(1923).—A review of the literature showing the effect on the tanning properties of tanning materials due to physical changes of their constituents. J. A. WILSON

**The behavior of amino acid in the presence of hide powder and tanning materials.** W. MÖLLER. *Z. Leder-Gerberie-Chem.* 2, 212-27(1923).—The adsorptive power of hide powder for tannin, HCOH, and Cr alum is lessened by the addn. of NH<sub>2</sub>CH<sub>2</sub>COOH to their solns. ERWIN J. KERN

**Utilization of Acacia decurrens in India.** C. E. MACKENZIE. *Science and Industry* 1, 430-2(1919); *Bull. Agr. Intelligence* 11, 589-90(1921).—The bark of this tree may be used for the manuf. of com. tanning ext.; it has the following compn.: tannin absorbed by skin 42.3%, sol. non-tannins 10.8%, insol. substances 34.1%, water 12.8%. The wood contains 7.7% water and yields on destructive distn. charcoal 32.0, tar 9.0, total AcOH 5.58, MeOH 1.43%. JOSEPH S. HEPBURN

**Conditions affecting the hydrolysis of collagen to gelatin.** R. H. BOGUE. *Ind. Eng. Chem.* 15, 1154-9(1923).—In converting collagen into gelatin, the  $p_H$  value should be maintained either between 3 and 4 or between 7.5 and 8.5. Between the values 4.5 and 6.0, hydrolysis proceeds too slowly, while at values below 3 or above 8.5 the gelatin formed rapidly breaks down. It is best to use about 12 parts of water to each part of dry collagen and to keep the temp. at 80° for about 8 hrs. A fine cutting of the stock and const. agitation permit lowering the temp. to 75° and the time to 6 or 7 hrs. Previous swelling of the stock may best be done with lime or lactic acid, but excess of the reagent must be removed before heating to insure the best results. Collagen appears not to be a simple anhydride of gelatin, but rather a polarization complex produced by chem. condensation. J. A. WILSON

Determination of Cr in the presence of organic matter (GRASSER) 7.









